The Institute of Paper Chemistry

Appleton, Wisconsin

Doctor's Dissertation

A Study of the Effects of Hydroxyethylation of Fibers on the Bonding in Paper

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June, 1968

A STUDY OF THE EFFECTS OF HYDROXYETHYLATION OF FIBERS ON THE BONDING IN PAPER

A thesis submitted by

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of The Institute of Paper Chemistry
for the degree of Doctor of Philosophy
from Lawrence University,
Appleton, Wisconsin

June, 1968

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SUMMARY

A study was made to gain an increased understanding of the mechanism by which chemical modification effects increased paper strength. Comber pulp, prepared from raw combers, was presteeped in 5% (w/w) alkali and then hydroxyethylated under vacuum with ethylene oxide to three different levels. The unmodified and hydroxyethylated pulps were classified on the IPC Web Former. Unbonded, water-dried fibers of the samples were prepared also using the IPC Web Former. Handsheets were prepared on a newly built IPC constant-rate sheet former.

Test results showed that changes in fiber length distribution, formation, and fiber strength due to hydroxyethylation treatment did not contribute to the observed increases in paper strength. Increases in fiber-fiber bonding appeared to be almost entirely responsible for the increase in strength.

The percentage relative bonded area of the hydroxyethylated pulp handsheets, calculated from the gas sorption areas of the unbonded, water-dried fibers and of the handsheets, showed a maximum increase of 40% over the untreated control. The specific bonding strength values, obtained by division of the IPC bonding strength value by the percentage relative bonded area, increased progressively on hydroxyethylation. The maximum increase in this case over the untreated control was around 700%. Based on the maximum effects, the changes in percentage relative bonded area contributed less than 10% and the changes in specific bonding strength, more than 90% to the increased strength in paper.

The Nordman bonding strength values also showed considerable increases on hydroxyethylation, the maximum increase being around 185% for the optical method and around 100% for the gas sorption method.

Hydrodynamic properties of the handsheet pulps showed continual increases in the compressibility constant, M, and a decreasing trend in the hydrodynamic surface, S_w, with increased degree of hydroxyethylation. The specific volume, V, decreased significantly with the first addition of ethylene oxide.

The gas sorption areas of the unbonded, water-dried fibers decreased with hydroxyethylation. The modulus of elasticity, E, of dry fibers decreased on hydroxyethylation. The hydroxyethylated pulp handsheets showed increase in density as well as Bendtsen porosity and average pore size.

The hydroxyethylated fibers appeared more translucent than the unmodified fibers. Under the microscope, the hydroxyethylated samples from the mercury-intruded handsheets had considerably fewer fibers with lumens filled with mercury than the unmodified samples. Electron micrographs of the hydroxyethylated pulp handsheets showed a more conformed structure and a much less distinct aggregation of microfibrils than those of the unmodified pulp handsheets. The surfaces appeared smoother and of granular type for the hydroxyethylated fibers.

These considerations have been interpreted to indicate a high shrinkage potential and an increased deformability of the fibers and fibrils on hydroxyethylation. Effects of 5% alkali alone were either insignificant or adverse in the present study. Hydroxyethylation seems to provide a "built-in plasticizer," making the treated surface smoother and more conformable. This then provides extensive molecular contact and increased response to the Campbell effect during sheetmaking. The fines (through 65- but retained on 200-mesh) promote the action of hydroxyethylation. They become more highly substituted than the longer fiber fractions during hydroxyethylation. These highly substituted fines can then act as an additive.

INTRODUCTION

Almost since the beginning of papermaking, man has tried several ways to improve the strength of paper. Subjecting the fibers to mechanical action such as beating is the oldest and most common. Another way is to add nonfibrous materials as beater additives to pulp suspensions. Chemical modification assumes importance in papermaking also because of its ability to effect substantial increases in paper strength.

Cellulose is a linear high polymer. The repeating unit in the cellulose chain is anhydro-D-glucose, having the empirical formula $C_6H_{10}O_5$, joined by beta 1, 4-glucoside linkages. The structural formula of cellulose is shown in Fig. 1.

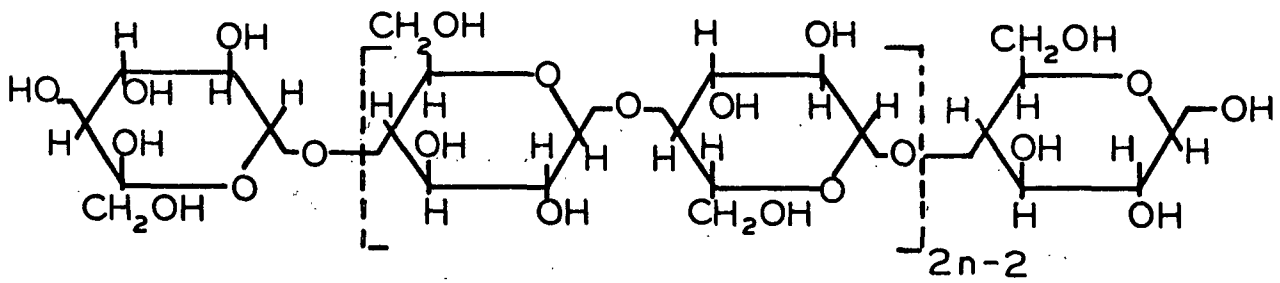

Figure 1. The Structural Formula of Cellulose

There are three principal ways in which cellulose can react. First, the glucosidic linkage can be attacked, as is the case in hydrolysis and some other degradations. Second, the hydroxyls can be oxidized or substituted in various ways. Third, the C-H bond or other low-energy bonds can be broken, as by high energy radiation.

In chemical modification of the papermaking fibers, the interest is in the hydroxyl groups of the cellulose. Each anhydroglucose unit contains three hydroxyl groups; there may be up to 10,000 or more hydroxyl groups per cellulose molecule. These are the groups responsible for esterification and etherification reactions. In the case of hydroxyethylation of cellulose by ethylene oxide, the hydroxyethyl group (- CH_2CH_2OH) can be introduced into the cellulose molecule in two ways. First, ethylene oxide reacts at the hydroxyls in the cellulose chain. Second, ethylene oxide, reacting at previously substituted hydroxyls, can polymerize to form a side chain. The number of hydroxyl groups per anhydroglucose unit that is substituted is known as the "degree of substitution" or D.S. The average number of moles of ethylene oxide that become attached to each anhydroglucose unit in the two ways is called moles of substituent combined, or M.S. Figure 2 illustrates this distinction.

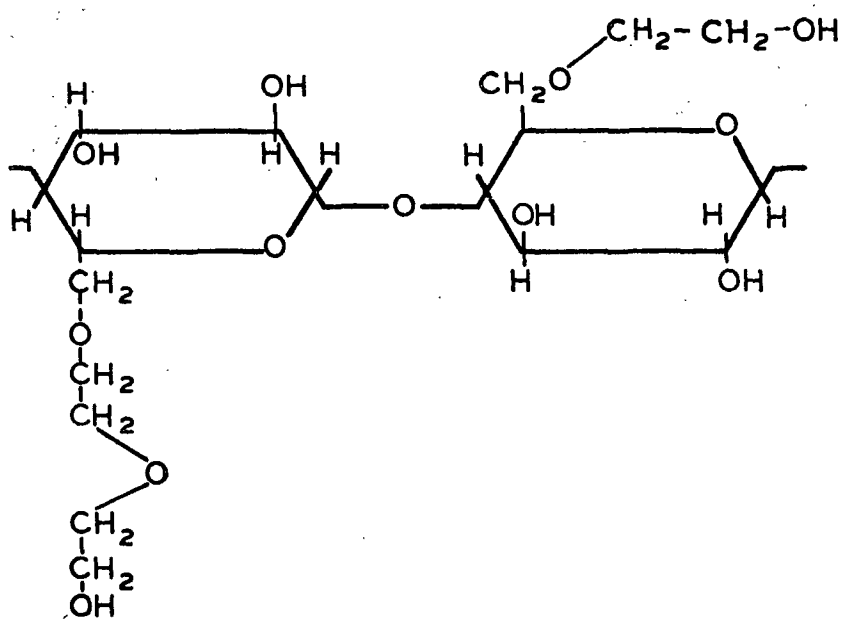

Figure 2. Fragment of a Partially Substituted Hydroxyethyl Cellulose (D.S.-1.0; M.S.-1.5)

CHEMICAL MODIFICATION OF PAPERMAKING FIBERS

Chemical modification usually implies a low, partial substitution of the hydroxyls of the cellulose fiber. There are many types of chemically modified fibers which have been investigated for use in paper – partly acetylated fibers, cross-linked fibers, cyanoethylated fibers for heat resistance and electrical insulation, graft polymers, diketene-sized fibers, reactively dyed fibers, etc. These may involve the hydroxyls of cellulose – in one or several of these ways – monosubstitution, polysubstitution, and grafting. The monosubstitution reactions have been known for many years to improve the strength properties of pulps and papers.

Jayme and Froundjian (1) in 1940 partially methylated an unbleached sulfite pulp. They increased the methoxyl content of the pulp from 1.59 to about 9%. The methylated pulps on beating produced handsheets 50% stronger in bursting strength than the sheets from unmethylated pulps. The partially methylated pulps also showed 50% increase in water-binding capacity as compared to the untreated pulp.

Later, and independently, Bletzinger (2) studied the effects of acetylation. He prepared a series of pulps with acetyl contents varying from 4.25 to 26.46%. When handsheets were made from these unbeaten pulps, the strength properties of the sheets decreased as the acetyl content increased. Even an acetyl content of 4 to 6% was enough to reduce the water-binding capacity of these fibers and the strength of the resulting sheets. However, when these pulps were beaten, the fibers with acetyl contents below 8 to 9% formed sheets with strength properties greater than sheets prepared from untreated fiber. The maximum burst increase of about 10% occurred at an acetyl content of about 6%. Acetylation above 9% decreased

the swelling by water so much that poor bonding was obtained and satisfactory sheets could not be formed with water.

Aiken (3) confirmed the results of Bletzinger using another rag stock and a bleached Mitscherlich pulp, and also a milder acetylation procedure to obtain the pulps of low acetyl contents. He found a maximum increase in the strength properties of the acetylated rag stock at an acetyl content of about 3%. He then measured the hygroscopicity of dried acetylated pulps and found a maximum also at an acetyl content of about 3%. The curves of bursting strength versus acetyl content and hygroscopicity versus acetyl content were found to be similar.

Aiken also found that while the addition of xylan to rag stocks resulted in an increase in the strength properties of the resulting sheets, the addition of the acetylated xylan caused a decrease in the strength properties.

Harrison (4) corroborated the results of Aiken and Bletzinger. McKenzie and Higgins (5) obtained similar results on eucalyptus pulp, the breakpoint being around 7% acetyl content. More recently, Herdle and Griggs (6) have reported that papers made from partially acetylated cellulose containing ca. 20 acetyl groups are more stable to heat and light and have greater affinity for organic materials. In addition, these papers have better wet strength and dimensional stability. The water-absorbing tendency of the cellulose is reduced upon progressive acetylation of the hydroxyl groups.

Walecka (7) in 1956 first showed that pulps chemically modified to extremely low degrees of substitution (D.S.) with hydrophilic reagents and still insoluble in any solvents except those for cellulose were superior for papermaking. He carboxymethylated rag pulps in alcoholic media to obtain low-D.S. carboxymethylated cellulose (CMC) pulp fibers varying in D.S. from 0.006 to 0.06. Such treated pulps

produced stronger sheets than untreated rag pulps and also refined much faster. Up to about 0.06 degree of substitution, there was a rapid increase in the burst and tensile strengths and a slight increase in the tearing strength. He also observed an increase in the zero-span tensile strength of the fibers. The opacity and the porosity of the handsheets were decreased as the D.S. was increased. The equilibrium moisture content of the treated pulps was higher. Photomicrographs showed that the beaten CMC pulp contained more transparent fibers than did the untreated pulp.

These results were further confirmed by Talwar (8). Ward, et al. (9) and Nelson, et al. (10) discuss conditions of carboxymethylation as an important factor in improved strength properties of paper sheets made from the treated fibers.

Harpham, et al. (11) describe cyanoethylation, carboxymethylation, hydropropylation, and hydroxyethylation to produce improved papermaking properties. Spadaro, et al. (12) of the Southern Regional Research Laboratory have also described hydroxyethylated and cyanoethylated fibers. Baker and Sepall (13) report that carboxyethylation improved strength of sheets made from poor papermaking fibers. Also a remarkable stability to repeated drying, even at elevated temperature, was reported. A more general study of handsheet properties for pulps made from second-cut cotton linters chemically modified by a wide range of treatments has been reported by Ward and his coworkers (14).

A great interest has been shown in chemical modification by hydroxyethylation. Apart from the economic reasons, which have made hydroxyethylated linters a commercial product, one important reason is that the hydroxyethylated pulp is less sensitive to electrolytes in the papermaking system than carboxymethylated pulp. Richter, in 1936 (15), patented the formation of paper from alkali-soluble

hydroxyethyl cellulose. A. W. Schorger (16) in 1950 prepared stereotype mats from hydroxyethyl cellulose of a degree of subsitution of 0.25 to 1.5. Harpham (17) in 1957 obtained a U.S. patent on the improvement of the strength of paper by etherifying the cellulose fibers (primarily cotton linters) to obtain a hydroxyethyl cellulose of D.S. not in excess of 0.2. Klenkova and her coworkers (18) in a recent paper have observed high swelling power and high water-binding capacity in low D.S. hydroxyethylated cellulose (HEC). They experimented with HEC fibers with a content of hydroxyethyl groups not exceeding 8%, which were prepared from mercerized cotton cellulose. It was found that low D.S. HEC is characterized by low density and a large internal surface area, as compared with native cellulose and mercerized fibers. The x-ray diffractograms indicated that the above HEC fibers had an amorphous structure. Akim, et al. (19) have shown that low-substituted HEC retains the fibrillar structure of the fibers, but the fibrillar bundles are intertwined forming a network with highly developed surface. The modified fibers are beaten more easily than the native fibers, and paper handsheets show higher strength values. Thomas (20) prepared hydroxyethylated fibers from mercerized but undegraded cellulose. These fibers resisted beating but developed high strength. They had the cellulose II crystal structure but were pliable and swelled rapidly in water. They fibrillated with a stringier, more layered appearance than normal fibers, and formed open but highly bonded sheets with good brightness retention properties. The work at The Institute of Paper Chemistry is the most comprehensive on hydroxyethylation and continual increase in the strength properties is observed with increasing degree of hydroxyethylation up to about 0.312 (21,22,22a).

All of these treatments suggest that the effects of chemical modification at low degrees of substitution are general and can be obtained by treatment with more than one type of small group (methyl, acetyl, carboxymethyl, hydroxyethyl, etc.).

At such low degrees of substitution, the qualitative phenomenon occurs regardless of the nature of the substituent group. For instance, the hydrophilic groups in carboxymethyl cellulose and the hydrophobic groups in the others display similar phenomena at low degrees of substitution. A greater amount of hygroscopicity is observed in both cases, and handsheets from the low-substituted pulps display higher strength. A detailed explanation of the mechanism producing increased strength is still lacking.

PRESENTATION OF PROBLEM

The strength of a sheet of paper, as measured in a conventional tensile tester, is believed to depend on a number of factors (23). A sheet of paper is a three-dimensional network of fibers which are attached to one another. The strength of this structure can be attributed partly to the strength of the building elements (fibers) and partly to the strength of the bonds between the elements. Also, the strength of the structure will be dependent upon the distribution of the bonds, in other words, the formation.

The importance of fiber strength in the strength of paper has been well established by Van den Akker, et al. (24). They have demonstrated that substantial percentages of fibers fail during a tensile test, even in papers made from only moderately beaten pulps. Leech (25) has shown that an increase of 20 Thwing units (from 21.9 to 43.0) in formation values (obtained by addition of locust bean gum in pulps) gave a 40% increase in bursting strength and a 24% increase in tensile strength. A major portion of the strength of paper is, however, related to the fiber-fiber bonding in the sheet. These bonds are not due to mere mechanical entanglement of fibers. The type of bonds which contribute so greatly to paper strength are a result of accumulative secondary valence forces, primarily hydrogen bonding. In this respect, Swanson (26) has listed four important facts:

1. Hydroxyl groups viewed on a molecular scale are strongly polar.
2. Papermaking pulp fibers have a multitude of hydroxyl groups which are potentially capable of interaction by the orientation effect.
3. The attractive forces mentioned above decrease with the inverse seventh power of the distance. Therefore, elements of the fiber surface which are to be bonded together must approach one another very closely if these forces are to become effective. The distance of separation should be no more than a few angstrom units.

4. Rigid solid surfaces are very rough, and the real area of contact on a molecular scale when two such rough surfaces are brought together is very small.

From these facts, it is evident that the fibers must be brought into intimate contact on a molecular scale for good fiber bonding.

Campbell (27), Van den Akker (28), Fineman (29), and Lyne and Gallay (30) have all contributed a great deal to this understanding. Briefly, the formation of bonds is explained as follows: As the fiber suspension reaches about 25% solids, the individual fibers are no longer surrounded by large regions of water, but adjacent fibers almost in contact will be separated by thin layers of water. As drying continues, the water layer will shrink, drawing these adjacent fibers together with pressures in excess of 100 atm. to a sufficiently close proximity for hydrogen bonding to occur. This phenomenon has been referred to as the "Campbell Effect".

Anything that assists in the "Campbell Effect" will produce increased bonding and, therefore, corresponding increased strength in paper. The presence of highly swollen, amorphous regions in cellulose fiber (2,31) and the presence of hemicellulose (32-35) contribute greatly to bond formation by increasing the surface area and deformability of the fiber mat. Beating and refining also tend to increase swelling and surface area, thereby improving strength properties associated with fiber binding. Also, most of the traditional wet-end and beater additives act to "advance the cause of beating" (36).

Many investigators (2,8,21) have offered similar explanations for the effects of chemical modification on fibers, which can be summarized as follows: The effect of introducing a hydrophobic group like acetyl into the cellulose molecule is a physical distortion of the fiber structure. Below a critical maximum degree

of substitution which is low in value, additional cellulosic hydroxyls are exposed. The substituent group itself does not enter into normal interfiber bonding. If the substituent group is hydrophilic rather than hydrophobic, it can be assumed to participate in interfiber bonding. In any case, the fibers have much greater affinity for water, particularly in the modified regions. The wet fiber is studded with small regions where water has penetrated and separated the molecules by solvation and swelling. At these points there is increased mobility of the molecular segments and increased flexibility of the wet fiber. This persists during the early stages of drying, improving the capacity to form hydrogen bonds both within the fiber and between fibers, for the hydroxyl groups draw together on drying because of movement of the molecules and deformation of the fibers.

The increased fiber-fiber bonding may result from two principal effects: one, from an increase in the bonded area as related to the total available area for fiber-fiber bonding (referred to as relative bonded area in the paper); and two, from an increase in the bonding strength for the same bonded area (referred to as specific bonding strength).

In order to calculate the strength of bonds, Nordman, et al. (37,38) introduced a new approach. In the definition of bond strength, they thought in terms of energy and not in terms of force. They made use of the fact that when paper is strained and bonds fail, the area of cellulose-to-air interfaces in the sheet increases. The energy consumed in straining the sheet can be determined from the area of the hysteresis loop of the stress-strain curve. A plot of the change in area against the irreversible energy loss can then be made. The Nordman bonding strength is defined as the cotangent of the angle of inclination. Thus, the average bonding strength of a sheet of paper is defined as the irreversible work in ergs per gram of paper necessary to increase the measured area by one square

centimeter. The assumption of Nordman's work is that energy is consumed only by breaking of fiber-fiber bonds. Van den Akker has indicated that the Nordman value "is a force-limited irreversible energy absorption in the paper structure (per gram of fiber), the force being the failing force of fiber-fiber bonds" (39). He has theoretically calculated on a rough basis the order of energy required to break bonds in an area of 1 $cm.^2$. His figures are of the order 20-25 $ergs/cm^2$. against a Nordman value of the order of 2.2×10^4 $ergs/cm.^2$ (gas sorption area). The bulk of the energy, therefore, must go to sources other than bond breaking. However, the concept of Nordman bonding strength may be important for papermaking pulps. They have been reported to be independent of beating and wet pressing, particularly in pulps of low hemicellulose content (37,38). It increases, however, with increasing pentosan content.

The objectives of the present study were an increased understanding of the mechanism by which chemical modification of fibers effects increases in the strength of paper. An outline of the program is presented in Fig. 3.

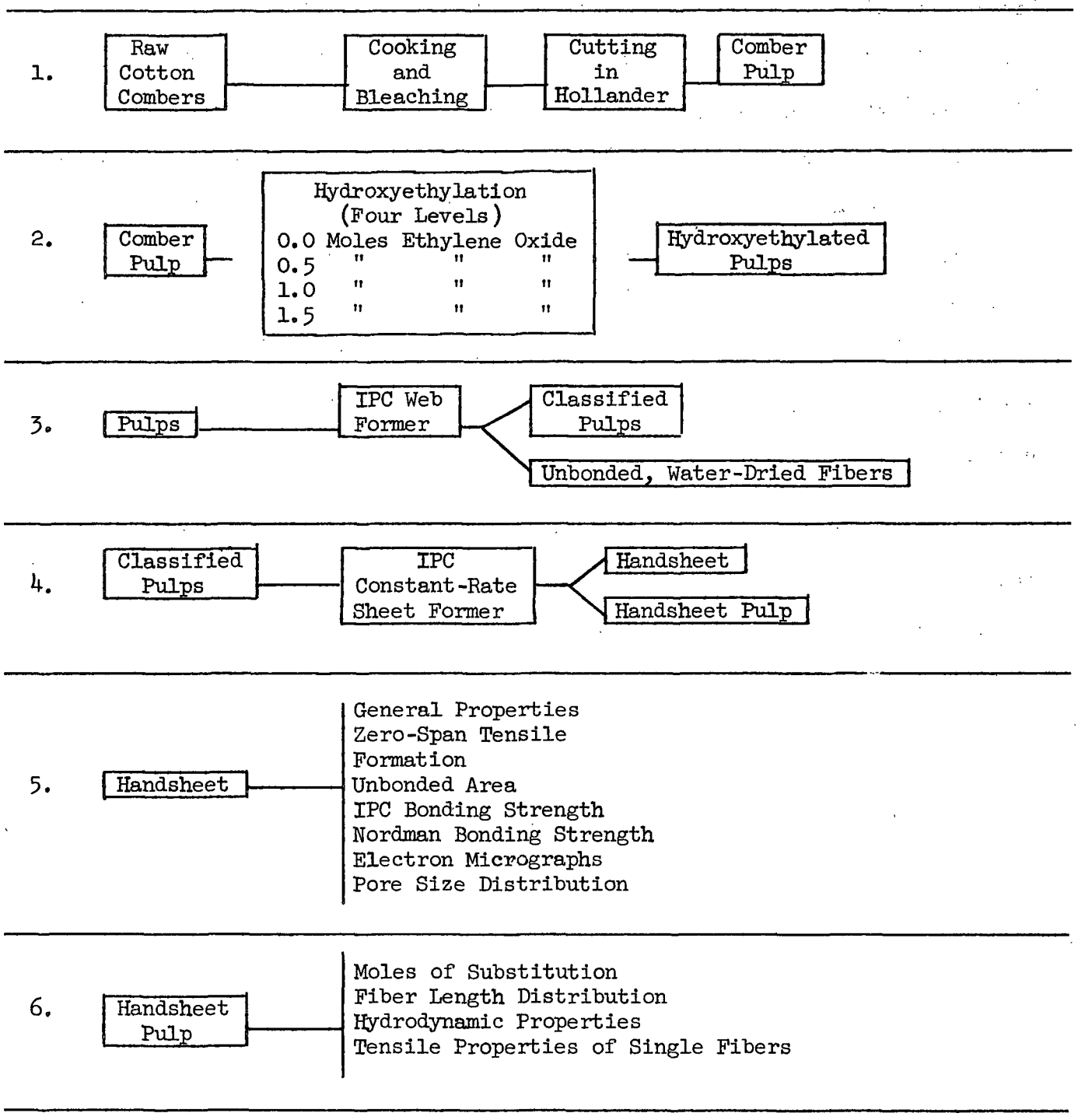

Figure 3. Outline of Program

EXPERIMENTAL

PREPARATION OF COMBER PULP

Cotton combers are lint fibers which go to the textile industry but are combed out at the carding operation as unsuitable. They were selected for the present study because they contain only minor amounts of noncellulosic material and have not undergone any essential chemical or mechanical treatment.

Raw combers were cooked using steam at 45 p.s.i. in a rotary boiler for 4 hours with 2% caustic. The cooked combers were put into hollanders and washed. They were then cut under heavy load on the rotor bars, and bleached with high test hypochlorite (70% available chlorine on a weight basis) at a level of 2.3 kg. per ton. Excess bleach was washed out. The stock was allowed to drain overnight. Then the stock was centrifuged and shredded in the IPC shredder and put into a large polyethylene bag. A few drops of formaldehyde were added to the fibers and then they were stored in a cold room at 40°F.

HYDROXYETHYLATION OF COMBER PULPS

For each sample 2250 g. (ovendry) cotton combers and 35 liters of 5% (w/w) alkali were used in the preparation of soda cellulose. This was done in a 70-liter stainless steel container where the comber sample was submerged evenly. Steeping with the alkali was for thirty minutes duration. Temperature was not controlled in the steeping process. After steeping, the mass was emptied into a nylon cloth bag and placed in a centrifuge. Here the soda cellulose was freed from the liquor to a press-weight ratio (ratio of the weight of the pressed soda cellulose to the weight of the original pulp) of 2.8-2.9.

The soda cellulose was then shredded on the IPC shredder and placed in a 55-gallon stainless steel drum. A vacuum of about 23-27 inches of mercury was applied. The drum was shaken and rotated to distribute the sample evenly across the drum, which was lying on its side. It was then mounted on trunnions. Equivalent moles of liquefied ethylene oxide for the respective samples were at once admitted to the soda cellulose. The drum was rotated continuously on the trunnions at a speed corresponding to twenty three seconds per round, for a period of two hours. At the end of the period, a vacuum of about 10-23 inches was still prevailing in the drum. No increases in temperature were observed.

The hydroxyethylated combers were washed exhaustively with deionized water, neutralized with dilute acetic acid and then washed electrolyte-free. This was done in the centrifuge. The combers had a dry fiber content of around 33-38% at which they were placed in polyethylene bags. A few drops of formaldehyde were added and then the samples were stored in a cold room at 40°F.

CLASSIFICATION OF PULPS

The unmodified and hydroxyethylated pulps were classified on the IPC web former. The IPC web former is a small paper machine, having a maximum speed of about 50 f.p.m. The usual speed of operation is in the range of 5-25 f.p.m. The web former has a deckle of 12 inches and is designed to produce a continuous web under controlled conditions.

Basically, it comprises a flow spreader and a vacuum forming system with a conventional white water and stock supply system (Fig. 4). The operation is similar to that of a paper machine. The stock is beaten to the desired freeness and pumped to the stock chest. This is then metered through a magnetic flowmeter to the wire pit. There it is diluted to the desired consistency. This low-consistency stock is then metered through an orifice to the flow spreader.

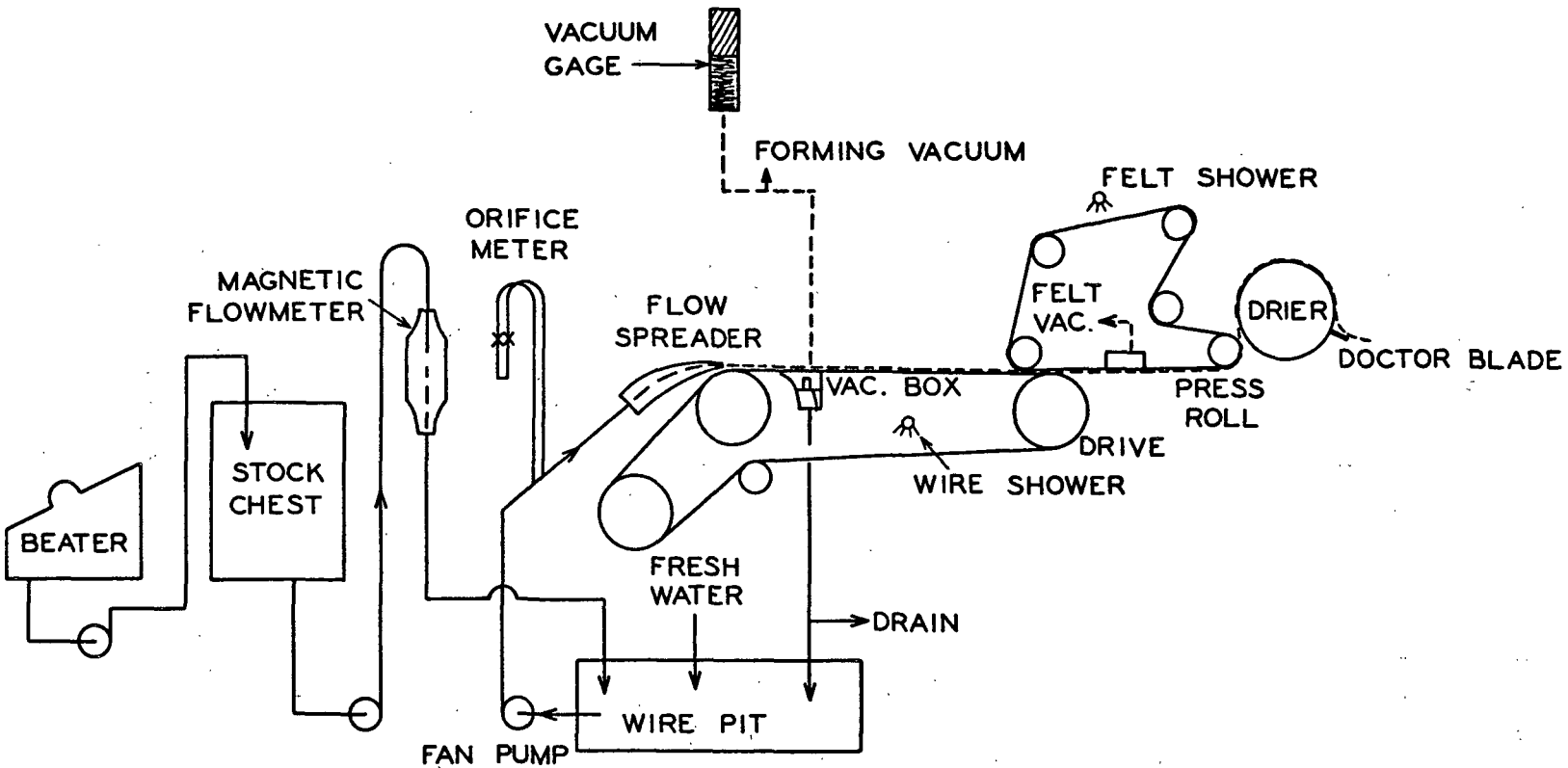

Figure 4. Schematic Diagram of IPC Web Former

The web is formed on the wire (72 x 56 mesh and twill weave) under vacuum. Drainage control is achieved by varying the vacuum on the forming section. Quite a wide range of drainage velocities is possible with this system, ranging from very low to those comparable to modern high-speed machines. The white water system can be operated at various degrees of closures. The web is picked up from the wire by a vacuum felt system and then transferred to the drier section. In this study, only one of the two small Yankee driers was used and the web was collected with the help of a doctor blade on this drier. The adhesion between the web and the drum was so weak that doctoring produced no deleterious effect.

For each sample 681 g. (ovendry) fibers were slurried in the beater for 5 minutes with no load. The slurry was then pumped into the stock chest of the IPC Web Former, and filled with water up to a premarked height. The slurry was air agitated, and then run through the Web Former at a consistency of about 0.004% and collected on a cold drier drum with the help of a doctor blade. The pulp was then again slurried in the beater and run over again on the IPC Web Former. The pulp was then centrifuged and passed through the IPC-shredder twice, put in polyethylene bags with a few drops of formaldehyde and stored in a cold room (40°F.).

PREPARATION OF UNBONDED, WATER-DRIED FIBERS

An extensive preliminary study was undertaken to develop a method of preparation of unbonded, water-dried comber fibers on the IPC Web Former (Appendix I). In this method, the fibers go across the wire as individual entities and are couched from the wire on the drier drum, where they dry and are collected. The method eventually gave clean fibers essentially unbonded and free from knits and creping. (Knits and creping are illustrated in Fig. 5 and 6.)

Figure 5a. Illustration of Knits (Identification A) in Dry Mounting, Bright Field Illumination at 150X

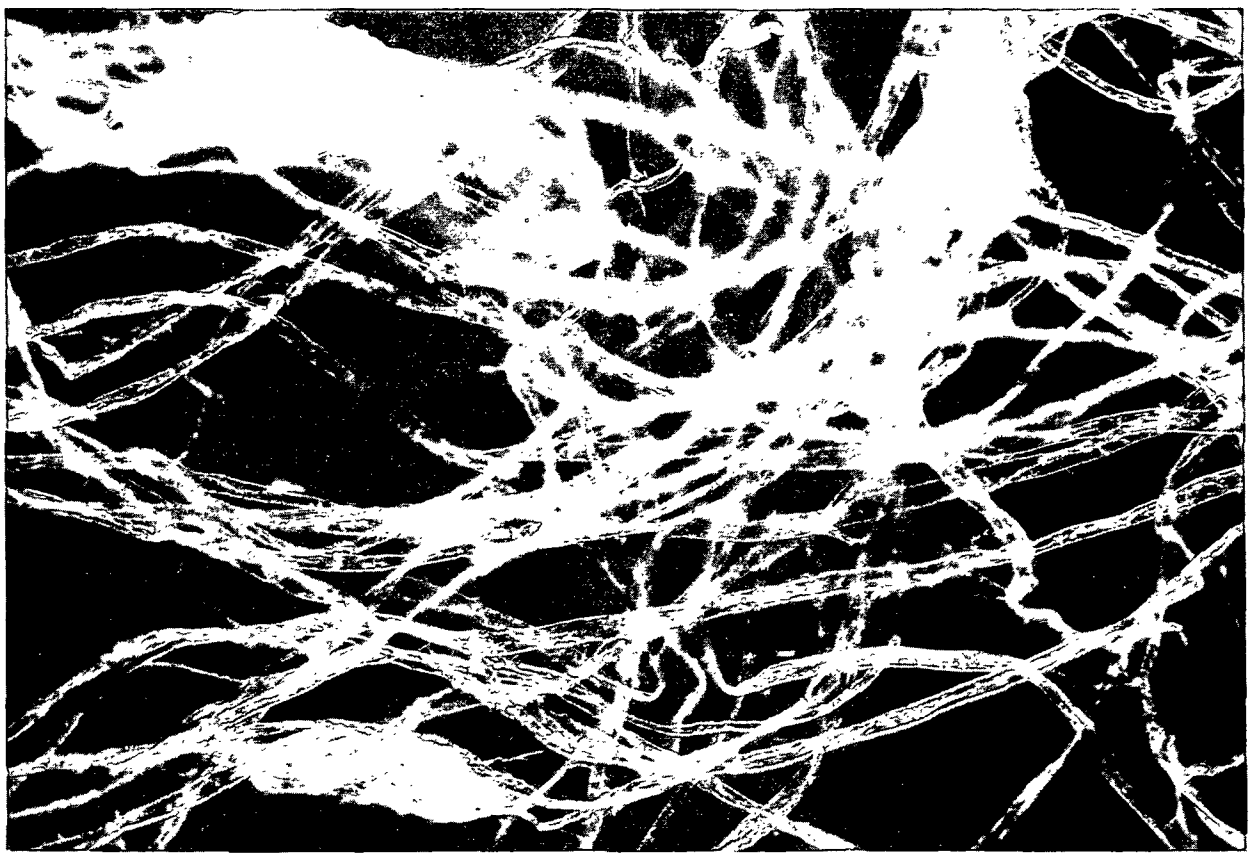

Figure 5b. Illustration of Knits (Identification A) in Dry Mounting, Dark Field Illumination at 150X

Figure 6a. Unbonded Fibers (Identification C) in Dry Mounting, Bright Field Illumination at 150X

Figure 6b. Illustration of Creping (Identification C) in 'C'-Stain at 375X

For each sample, 15 g. (ovendry) fiber was taken in 2000 ml. deionized water and disintegrated for 600 rounds in the standard disintegrater. The slurry was transferred to the stock chest which was filled up to a mark, about 80 cm. high. The slurry was air agitated. This slurry was then run through the thoroughly cleaned Web Former system at a consistency of about 0.002% under the following conditions: speed of the Web Former – 32-40 f.p.m., stock feed 1.85 gal./min., inlet feed – 8 gal./min., nip pressure – 15-20 p.s.i., wire – 72 x 56 mesh. No vacuum was used on the wire for web forming. The felt was kept quite wet and quite clean. Only one drier was used. Steam at 5 p.s.i. was opened until the drier was warm and then the steam pressure reduced to less than 1 p.s.i. The fibers were removed from the drier drum with the help of a stainless steel doctor blade and put in a sealed container.

PREPARATION OF HANDSHEETS AND HANDSHEET PULPS

Cotton combers, in general, do not produce well-formed handsheets. Hydroxyethylated combers have the extra problem of sticking to the blotters on drying. A preliminary study was undertaken to improve the formation in handsheets prepared from cotton combers (Appendix II). In this study, a method was developed to use a newly built IPC constant-rate sheet former (Fig. 7 and 8). Using this method, it was possible to obtain formation values of 55 Thwing units as compared to 21 Thwing units obtained on the conventional British sheet-forming apparatus. Sandwiching the handsheets between millipore filters (Millipore Filter Corporation, Bedford, Massachusetts: 220 nm. pore size) during drying was found to be the best way to eliminate the problem of sticking of handsheets.

PREPARATION OF WATER

Softened water having pH 9.3, temperature 4 to 5°C., and hardness 0 p.p.m. $CaCO_3$ was available. This was modified by reducing the pH to 7.0-8.0 with sulfuric acid and by increasing the temperature to 20-23°C.

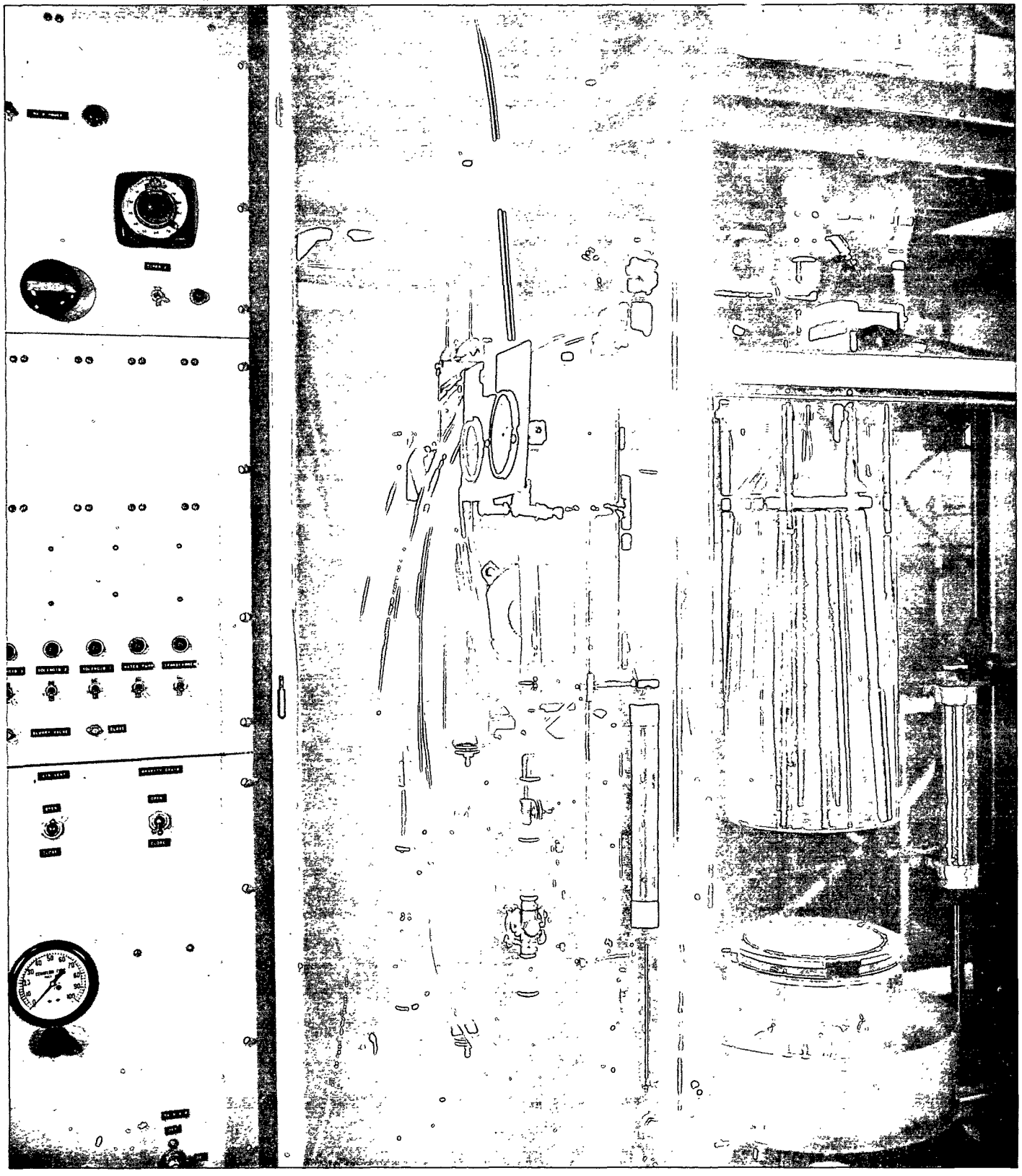

Figure 7. The IPC Constant-Rate Sheet Former

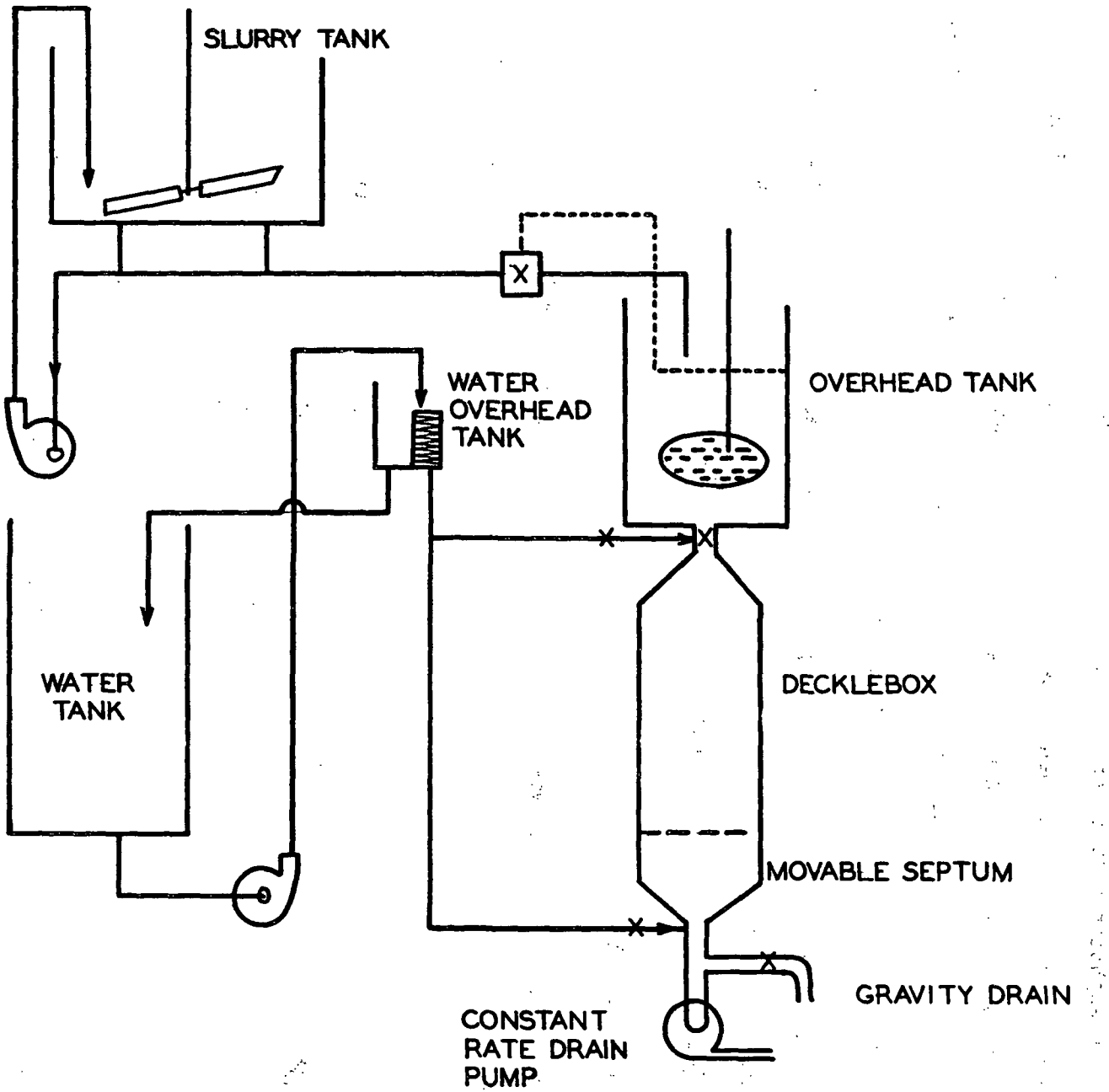

Figure 8. The Schematic Diagram of the IPC Constant-Rate Sheet Former

PREPARATION OF SLURRY

An eighteen-gram (ovendry) pulp sample was diluted with 2000 ml. of deionized water. This slurry was then agitated for 600 counts on the British disintegrator. The agitated slurry was then divided into two batches of 1000 ml. each. Each of the batches was then made up to 2000 ml. using deionized water and further agitated for 600 counts on the British disintegrator.

Pulp slurry consisting of 18 grams ovendry fiber in 4 liters of water was prepared this way and then added to the slurry tank containing 975 pounds of prepared water; the final consistency was 0.004%.

HANDSHEETMAKING

The overhead tank was filled with the pulp slurry and maintained at a constant level with the help of a level controller. The fresh water overhead tank level was also maintained through a continuous supply from the fresh water tank.

Fresh water was run in from underneath the septum. Entrapped air bubbles were taken out using localized suction. The septum was raised to connect to the deckle box, which was then filled up with water. During this time, the air vent of the deckle box was kept open. Air entrapped in the connection between the deckle box and overhead tank was vented out by opening the connection for a few seconds. Then the constant-rate drainage pump and the supply from the overhead tank were started simultaneously. The supply from the overhead tank was continued for a fixed predetermined period (usually 60 sec. for a 1.2-g. sheet) controlled by a timer. At the end of the period, automatically, fresh water was run in from the top of the deckle box and ran for a total of 20 seconds. At the end of 20 seconds, the constant-rate drainage pump stopped automatically. Immediately, the gravity drainage valve and the air vent were opened. After the water was drained, the

septum was lowered, the gravity drain valve closed, and the sheet was couched directly on a millipore filter.

COUCHING

The millipore filter paper backed with one thickness of a water-moistened Whatman No. 1 filter paper (moistened to minimize possible disturbance of the wet handsheet due to expansion of the filter paper) was laid centrally on the pulp sheet on the septum. Two blotters were then put on them. Then the flat brass couch plate was laid centrally on the blotters. The brass couch roll was placed gently on the middle of the plate. The roll was moved backward with no additional pressure to within less than 1/4 inch of the edge of the plate which was maintained horizontal by placing the fingers on the opposite edge, then forward to within less than 1/4 inch of the front edge, then back and forth again four times, and finally to the middle and then lifted off the roll. The time taken to perform the five complete rolls was about 20 seconds.

The pulp sheet, the millipore filter, the blotter, and covering brass plate were then removed from the wire in a manner similar to that of opening the covering of a book. Immediately one blotter and the brass plate were removed, and the rest of the combination was laid centrally, test sheet uppermost, over a mirror-polished plate, which was covered previously with a dry blotter. (The pulp sheet was marked at this stage for the couching direction and its wire side.) A millipore filter backed with one thickness of a water-moistened Whatman filter paper was then placed on top of the test sheet. Two blotters were then placed centrally on the test sheet. This was then covered with a mirror-polished plate and then with another blotter on top, placed centrally, ready to receive the next combination.

The next test sheet was made in precisely the same way. The maximum number of sheets that were pressed at one time was seven. Two blotters were laid on the

uppermost plate and two below the lowermost plate to avoid possible damage to the press cover.

PRESSING

The cover of the press was put on and the wing nuts were screwed down hand-tight. The pressure was then gradually raised over a total period of five minutes to 50 p.s.i., in increments of 10 p.s.i. applied over 1/2-minute periods, with 1/2-minute pauses between increments.

DRYING

The stack was removed from the press. The handsheets were then fitted into a set of drying rings with the millipore filters and Whatman filters in contact. Each sandwiched test sheet was centered carefully to be in contact with the rubber of the next ring. A heavy weight was placed on the top of the pile.

The sheets were allowed to dry in an atmosphere of 15 $\pm$ 2% relative humidity, and 73 $\pm$ 3°F. temperature in order to eliminate the drift in moisture content due to humidity cycling.

STORAGE

The dried sheets were then sealed in heavy polyethylene bags and stored in a dark place in an atmosphere of 50% relative humidity and 73°F.

Before use, the sheets were taken out of the bag and allowed to condition fully in an atmosphere of relative humidity 50% and temperature 73°F.

Handsheets for each sample were made in 4 batches (a-d). In all, about 40 handsheets were made for each sample. Three of them were of 1.0-gram weight, another three, of 2.4-gram weight, and the balance, of 1.2-gram weight. About 25

millipore filters were used for each sample as follows: batch (a) – fresh filters; batch (b) – filters from (a); batch (c) – filters from (b); batch (d) – filters from (c). The 1- and 2.4-gram sheets were made in batch (c). Usually each batch was pressed in two sets. Some additional handsheets of 1.2-gram weight were prepared as above but not subjected to pressing and drying. They are referred to as handsheet pulps.

Handsheets and handsheet pulps were prepared of the following samples:

C-U	Control,	untreated,	classified				
HE-0.0	"	Treated with	0.0	moles	ethylene	oxide[a]	Classified
HE-0.5	"	"	0.5	"	"	"	"
HE-1.0	"	"	1.0	"	"	"	"
HE-1.5	"	"	1.5	"	"	"	"
HE-1.5-uncl.	"	"	1.5	"	"	"	Not classified

[a]Moles per mole of anhydroglucose unit.

TESTING PROCEDURES

MOLES OF SUBSTITUTION

Samples were dried in air and at 38°C. in vacuo. Determination of the hydroxyethyl groups was done by the Morgan Method (40). This method uses hot, constant-boiling hydriodic acid to decompose the ethylene glycol residue quantitatively into a mixture of ethyl iodide and ethylene, which is collected and determined volumetrically in standard solutions of silver nitrate and bromine, respectively. In the present determinations, reaction time was 1 to 1-1/2 hours at 140-145°C. Duplicate determinations were made for each sample.

FIBER LENGTH DISTRIBUTION

The fiber length distribution determination was made for each sample using the Institute Fiber Length Recorder (41) based on the device described by Ilvessalo-Pfäffi and Alfthan (41a). The method is an optical projection method, according to which a stained fiber preparation is projected from below on a screen, using 50X magnification. The lengths of the fibers are measured from the projected image by means of the curvimeter of the fiber length recorder. The recorder divides the measured fibers into length groups, at 0.2-mm. intervals, and gives automatically the number of fibers in each group, as well as the total length and total number of the measured fibers. In the present case, the samples were stained with a saturated solution of Congo Red and diluted so that 1 cc. of the suspension contained approximately 100 fibers. A number of slides, each containing 2 cc. of suspension, were prepared from each sample. At least 1400+ fibers were so measured for each sample.

HYDRODYNAMIC PROPERTIES

The evaluation of hydrodynamic properties was done using the constant-rate filtration method of Ingmanson and coworkers (42-45). The latest version of this apparatus has been given on p. 176 in Ref. (45). A comprehensive discussion of the theory and method is also given there. The essential feature is to record the pressure rise during mat formation carried out at a known flow rate. From the known suspension consistency and flow rate, the basis weight of the mat at any time (discarding the initial period) is calculated from the fiber balance. The corresponding pressure drop across the mat is read from the recorded pressure-time curve, and corrected for the septum resistance.

Transformation of the Darcy equation relates the specific filtration resistance to the parameters of the system as indicated:

$$\overline{R} = \frac{\Delta P}{s\mu U^2 \rho t} \qquad (1)$$

where

$\overline{R}$ = specific filtration resistance

ΔP = pressure drop

s = consistency

ρ = density

μ = viscosity

U = velocity

t = time

From permeability considerations, Equation (1) may be correlated with mat density. Using the Davis-Ingmanson correlation of the Kozeny factor at lower porosities, the average specific filtration resistance is obtained as:

$$\bar{R} = k_1 \ (S_v^2/\rho f) \ (c/\rho_f)^{1/2} \ [1 + k_2(c/\rho_f)^3] \qquad (2)$$

where

k_1, k_2 = constants

c = mat density

S_v = specific surface area per unit volume of fiber

ρ_f = density of the fibers

To determine the hydrodynamic components of filtration resistance for cellulosic fibers, the differential constant-rate filtration equation may be arranged into a rectified and integrated equation of the form:

$$\frac{\Delta P}{\sqrt{c\ t}} = \frac{k_1(1 - N/2)S_w^2}{B\sqrt{v}} \ [1 + k_2 v^3(1 - N/2)^6 \ c^3] \qquad (3)$$

where

v = specific volume

N = number; compressibility power

B = filtration constant

S_w = specific surface area per unit mass of fibers

The compressibility can be represented by the simple power function:

$$c = MP_f^N \qquad (4)$$

where

M = compressibility constant

P_f = compacting pressure

In a filtration analysis, compressibility information was obtained from first compression data. The pulp slurry was added to the filtration tube and a pad was formed by the gradual downward motion of a permeable piston. Weights were added successively to the piston to compress the pad over a compacting pressure range of 8 to 147 cm. water. Pad thicknesses were measured with a dial micrometer.

Due to the viscoelastic properties of a fibrous mat, thickness had to be measured at some arbitrary time. The values of N were determined by measuring the slope of a plot of the logarithm of c as a function of the logarithm of compacting pressure. Then from a plot of the left side of Equation (3) against c^3 the value of the slope and the $c = 0$ intercept were used to evaluate the specific surface, S_w, and the specific volume, v.

GENERAL PROPERTIES OF HANDSHEETS

The randomized standard weight sheets were conditioned at 50% relative humidity and 73°F. (Institute Method 503) and subjected to the following tests (Table I).

TABLE I

TEST METHODS FOR GENERAL PROPERTIES OF HANDSHEETS

Tests	Institute Method	Units	No. of Readings per Sample
Basis weight	411	g./m.^{2}	10
Caliper	508	mm.	10
Density	508	g./cc.	10
B. & L. opacity	524	%	10
Burst factor	510	(g./cm.^{2})/(g./m.^{2})	18-20
Elmendorf tear factor[a]	512	g./(100 g./m.^{2})	7-8
Moisture at 50% R.H.[b]	411	%	1
M.I.T., double folds	513		20
Bendtsen porosity[c]	(46)	ml./min.	10
Instron tests[d]:			
Tensile strength (breaking length)		km.	10
Breaking stretch		%	10
Tensile energy absorption		kg.cm./cm.^{2}	10

[a] Tearing width parallel to the couching direction of the sheet.
[b] Strips cut perpendicular to the couching direction of the sheet.
[c] The Bendtsen smoothness and porosity tester, Model 6, was used at air pressure of 150 mm. of water. The directly observed scale readings were corrected on the basis of a calibration performed in the IPC laboratory.
[d] Instron tests: The Instron Universal Tester, supplied by the Instron Engineering Corporation, Canton, Mass., was used. Strips of one-inch width were used in the IPC line-type specimen clamps. The initial span length was 4 inches and the cross-head speed was 1 inch/min.

THE STRENGTH OF FIBERS

Two methods were used for measuring the strength of an individual fiber: the improved zero-span tensile test (47) and the IPC Fiber Load-Elongation Recorder (48).

The improved zero-span tensile test (47) is based on the concept of bringing special jaws in a tensile tester so close together that the measured results depend primarily on the strength of the individual fiber rather than on the bonding between them. Under properly controlled conditions, Van den Akker, et al. (24) have shown theoretically and experimentally that the zero-span tensile test indicates values equal to three-eighths of the average individual fiber strength in a sheet of paper. Ten disks of 0.756-inch diameter were cut out from a one-gram sheet. These sheets were weighed for basis weight. The disks were then tested on the Instron Universal Tester using the IPC zero-span attachment (47) at a loading rate of 6.35 kg./sec.

The more sensitive and accurate IPC Fiber Load-Elongation Recorder (48) was also used to measure the strength of fibers individually. As the method is time consuming, only three samples were tested. Single fibers were picked out with the help of a jeweler's tweezers from the undried handsheet pulp samples. Holding one end of the fiber with the tweezers, the fiber was laid flat on a Teflon-coated glass plate by drawing through a drop of water. The fiber was allowed to dry. When dried, the fiber ends were prepasted on the mounting pin using sodium carboxymethyl cellulose as the paste. The final gripping was done using Epon 907 epoxy resin (product of Shell Chemical Company) applied directly to the fiber at the pin ends. The glue was allowed to set overnight. The pair of pins was then mounted on the IPC Fiber Load-Elongation Recorder and subjected to stress under the following conditions: rate of loading – 0.69 g./sec.; span – 0.32 mm. The cross-sectional areas were calculated using the IPC Compacted Fiber Dimension Apparatus under a compacting load of 500 grams. They were done on a separate

batch of fibers and the average figure was used in calculating the breaking stress.

THE DISTRIBUTION OF BONDS (FORMATION)

The Thwing Formation Tester (49) was used here. The instrument measures formation by comparing the ratio of the variations in transparency to the average transparency.

THE UNBONDED AREA

Two methods were used to determine the unbonded area in handsheets: optical scattering method and gas sorption method.

OPTICAL SCATTERING METHOD

The optical properties of the samples were determined with the General Electric Reflectance Spectrophotometer (GERS) using light of 650-nm. wavelength. Twelve to eighteen measurements were made on each sample. The scattering coefficient was calculated from transmittance $\underline{T}$ and reflectance against black backing, $\underline{R}_o$, measurements. The instrument readings were changed to the absolute scale. The samples were then again conditioned at 50% R.H. and 73°F. and the basis weight was determined for each measuring point by punching out a 3.71 $cm.^2$ disk from the place where the optical measurement was made.

NITROGEN GAS SORPTION METHOD

The gas sorption surface areas were measured by using the Institute Modified Sorptometer and the dynamic gas sorption technique (50). All samples were conditioned at 50% relative humidity. For each sample, two tubes were loaded in a humidity-controlled room (50% R.H.) and the airdry weight of the sample in the

tube was determined. All the tubes were run together for each determination. A flow of 85% helium (carrier gas) and 15% nitrogen was used. The flow of the gas through the tube was about 13 ml./min. The areas under the adsorption and desorption curves were measured by a planimeter. The average value of adsorption and desorption was divided by the weight of the sample to give the sorption per unit weight. Whatman No. 1 filter paper was run as a standard (gas sorption area – 1.05 $m.^2/g.$) in order to calculate the absolute value of gas sorption areas.

The sample weights for the unbonded, water-dried fiber samples varied from 0.25 to 0.36 g. per tube. In the case of handsheets, the samples that were used for the optical measurements (minus the circles used for basis weight determinations) were cut to 4-mm. wide strips. Two bundles, each containing 25 to 35 strips, were loaded carefully, one above the other, into the tubes. The sample weights varied from 1.0 to 1.3 g. per tube.

THE STRENGTH OF BONDS

The strength of bonds was measured using two types of the transverse tensile tests: the IPC bonding strength test (yielding data on the "velocity-viscosity product") (51) and the improved z-direction tensile test (52). In the IPC measurement of bonding strength, a steel roller carrying a film of viscous oil is rolled over a test specimen with constantly increasing speed. The critical speed, that above which the test specimen suffers open rupture, was determined for each of various liquids of different viscosity. The product of velocity times viscosity has been shown to be constant, and this product is taken as a measure of bonding strength.

In the use of the improved z-direction tensile test, the test sample (120 $g./m.^2$) was cut into a disk about one square inch in area and glued between two cylinders of 1-1/4 inch height (area of 0.9903 $in.^2$) by Epon 907 adhesive.

After curing for at least 12 hours under 4 kg. compression, the excess of the specimen was trimmed off by razor blade from the steel cylinder. The cylinder was then attached to the clamp and tested on the Instron instrument using a crosshead speed of 0.1 in./min.

NORDMAN BONDING STRENGTH

For each sample, handsheets were cut in 11 cm. x 4.5 cm. strips — two from each handsheet. (All the strips were cut perpendicular to the couching direction of the sheet.) The strips from a sample were then randomized and divided into groups of six. One group was not strained, but the others were strained on the Instron to different strain levels. The Institute's line-type clamps were used. At each straining level, the six strips were strained up to a predetermined elongation and allowed to relax. The span length was 10.16 cm., specimen width — 4.5 cm., crosshead speed — 0.2 inch/min. and the chart speed — 5 inches/min. The load-elongation curves were recorded and the work done in loading and unloading was read from the integrators. (The integrator readings were corrected for backlash error.) After straining, the strips were taken out and cut to give that part of the specimen which was strained. This was then weighed. The maximum straining levels were 80 to 85% of the breaking stretch of each sample.

Three of the six strips from each strain level were randomly chosen. Along each strip, the optical measurements were done at three different points. In all, nine measurements were made for each strain level. After the optical measurements, the six strips for each strain level (minus the circles cut out for the basis weight determination in optical method) were subjected to gas sorption area determination using the technique as described under "The Unbonded Area."

PORE SIZE DISTRIBUTION

Pore size distribution was determined by the mercury intrusion method. The instrument was an Aminco Porosimeter, catalog no. 5-7121, which measured equivalent pore diameters from 100 nm. down to 0.012 nm. The theoretical basis for the mercury intrusion method is negative capillarity. In any system consisting of a porous solid and a nonwetting liquid, there is a free energy change resulting in a repulsion of the liquid from the surface of the solid. Pressure is therefore required to cause the liquid to enter any pore, and the pressure required is greater as the pores become smaller. This behavior is described by the following equation (53).

$$D = \frac{-4\gamma\cos\theta}{P} \qquad (5)$$

where

D = diameter (equivalent to cylindrical pore) of the smallest pore filled at pressure P

γ = surface tension of liquid

θ = wetting angle

P = applied pressure

For the mercury porosimeter the equation becomes:

$$D = \frac{175}{P} \qquad (6)$$

A sample of appropriate size was placed in a penetrometer (glass tube with graduated capillary stem). The penetrometer was placed in a filling device, evacuated and filled with mercury. Pressure and stem readings were taken as the system returned to atmospheric pressure. Pore diameters from 100 to 16 nm. were covered in this pressure range. The penetrometer was transferred to the pressure chamber. Pressure and stem readings were taken as pressure increased to the maximum of 15,000 p.s.i. Pore diameters down to 0.012 nm. were measured.

Corrections were made for the head pressure of mercury in the capillary stem, for mercury compressibility and for sample size. Pore size distribution was determined from the adjusted data for cumulative volume penetration, V, and absolute pressure. The term

$$\frac{\Delta V}{\Delta \log P}$$

was plotted against log P, giving a volume frequency distribution. In practice the volume and pressure data were smoothed by 3 points quadratic smoothing and values of $\Delta V/\Delta \log P$ were calculated with the IBM 1620 computer. Distribution curves were plotted using the Calcomp plotter. To indicate pore diameters instead of pressure the relation $\log D = \log 175 - \log P$ was used to set up a new scale.

MICROSCOPIC STUDY

PHOTOMICROGRAPHS

Fiber samples were prepared in distilled water and added to one-inch square areas on the ends of standard microscopic slides previously placed on a warm (60°C.) plate. The distilled water was allowed to evaporate giving samples in dry mounting. Also some samples were teased apart in "C"-stain without being wetted in water and without being dried on glass slides. Photomicrographs of some samples were prepared while using different conditions of illumination and magnification.

ELECTRON MICROGRAPHS

The direct replica method (54) as modified by Miss Smith (55) was used. The surface was shadowed by shooting palladium at an angle of 30° from heated tungsten. Carbon particles were then projected on top of the surface at right angles to the palladium film. The shadowed side of the specimen was then covered with a polystyrene disk. The combination was then subjected to vacuum. The cellulose was

dissolved out by acid hydrolysis (72% H_2SO_4). Then grids were glued onto the polystyrene disk replica and the polystyrene was washed out in benzene vapor. Grids were then examined under the electron microscope using a range of magnification.

RESULTS, DISCUSSION AND CONCLUSIONS

The extent of hydroxyethylation of the various handsheet pulps is shown in Table II. The physical properties of the handsheets prepared from these pulps are presented in Table III and some of the important ones are shown in Fig. 9-14. The limits wherever shown on data points on the graphs in the present study are of 95% confidence level. The hydroxyethylated pulp handsheets show a progressive increase (significant at 99% confidence level) in folding endurance, tensile strength, tensile stretch, bursting strength, and tensile energy absorption. The density of the handsheets increases and the B. & L. opacity decreases. Tearing strength at first increases and then decreases with increased degree of hydroxyethylation. In general, the effect of 5% alkali treatment alone is either insignificant or adverse.

TABLE II

MOLES OF SUBSTITUTION IN HANDSHEET PULPS

Sample Reference	Moles of Substitution[a]		
	Test 1	Test 2	Average
HE-0.5	0.084	0.079	0.082
HE-1.0	0.120	0.125	0.122
HE-1.5	0.220	0.219	0.220
HE-1.5-uncl.	0.229	0.236	0.232

[a] Basis: Moisture free (dried under vacuum over P_2O_5).
Reaction time 1 to 1-1/2 hours at 140-145°C.

Figure 15 represents a schematic sketch of the major factors and interactions involved in the development of strength of handsheets prepared from the hydroxyethylated comber pulp. Hydroxyethylation treatment can affect changes in one or more of the following factors: fiber length distribution, formation, fiber strength, surface area available for bonding, and bonding ability of surface.

TABLE III

PHYSICAL PROPERTIES OF HANDSHEETS PREPARED FROM UNMODIFIED AND HYDROXYETHYLATED PULPS

Moles of Subs. (M.S.)	Apparent Density, g./cc.	B. & L. Opacity, %	Burst Factor, $\frac{g./cm.^2}{g./m.^2}$	M.I.T. Double Folds	Breaking Length, km.	Stretch, %	Tensile Energy Absorption, g.-cm./cm.^{2}	Tear Factor, g./(100 g./m.^{2})	Moisture, %
Control	0.549±0.0031[a]	79.0±0.00	20.5±0.17	26± 0.7	2.78±0.036	3.0±0.10	43.8±2.09	247± 9.2	6.1
0.00	0.520±0.0038	79.5±0.21	18.0±0.16	15± 0.3	2.35±0.028	2.7±0.12	32.7±1.90	232±10.6	6.1
0.082	0.559±0.0034	75.0±0.15	24.5±0.24	31± 0.7	3.15±0.024	4.1±0.10	67.0±1.76	238± 9.4	6.3
0.122	0.552±0.0040	72.0±0.18	27.5±0.23	46± 1.1	3.31±0.048	4.6±0.15	78.5±2.90	273± 5.1	6.2
0.220	0.586±0.0049	69.5±0.17	36.5±0.24	110± 3.6	4.18±0.038	6.5±0.08	132.5±2.22	224± 3.0	6.1
0.232[b]	0.677±0.0055	70.0±0.41	50.0±0.69	500±32.0	5.56±0.077	7.8±0.10	205.8±4.30	163± 2.0	6.3

Basis: 50% R.H. and 73°F.

[a]Standard error.

[b]Unclassified pulp.

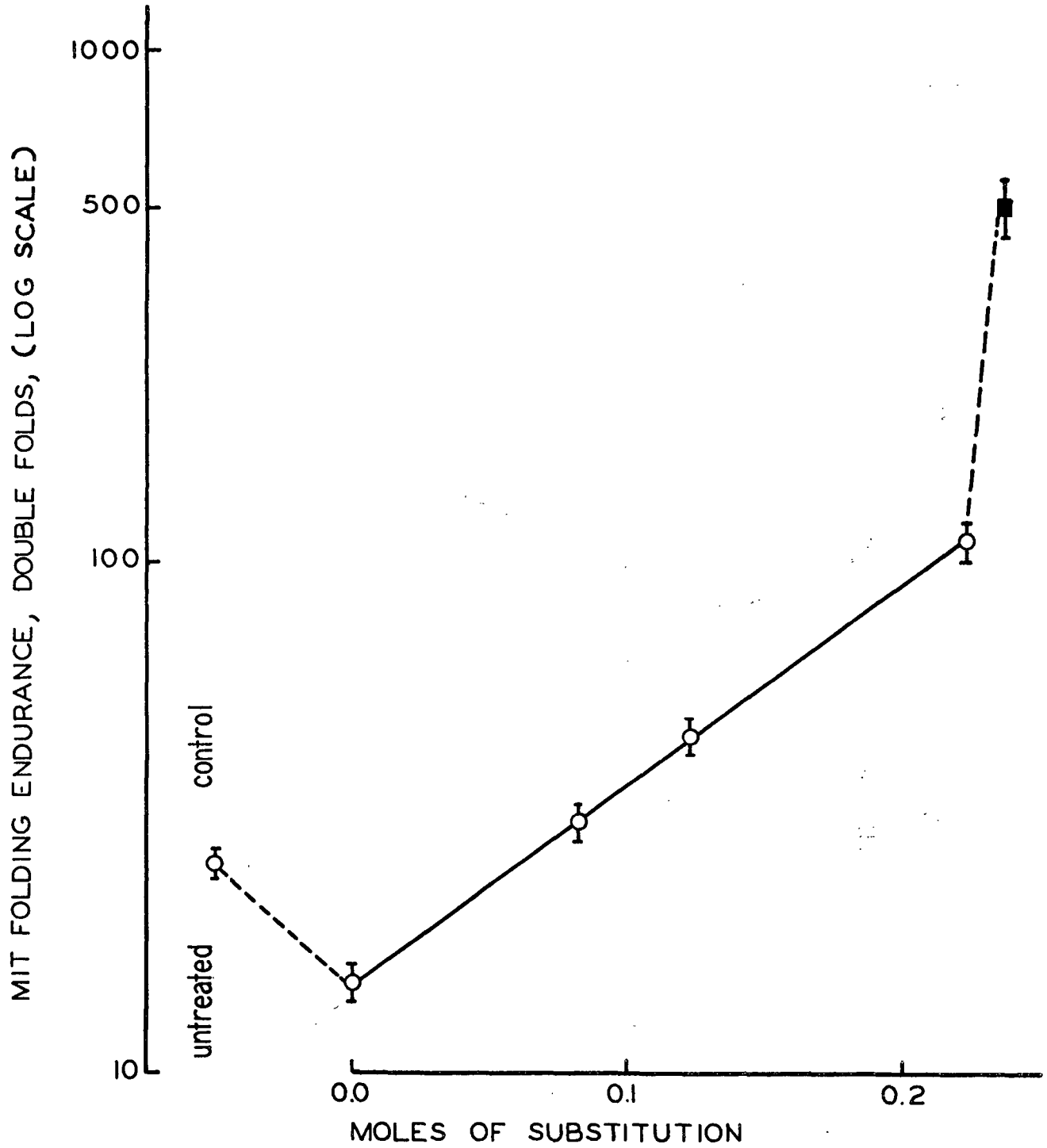

Figure 9. Effect of Hydroxyethylation on the Folding Endurance of Handsheets

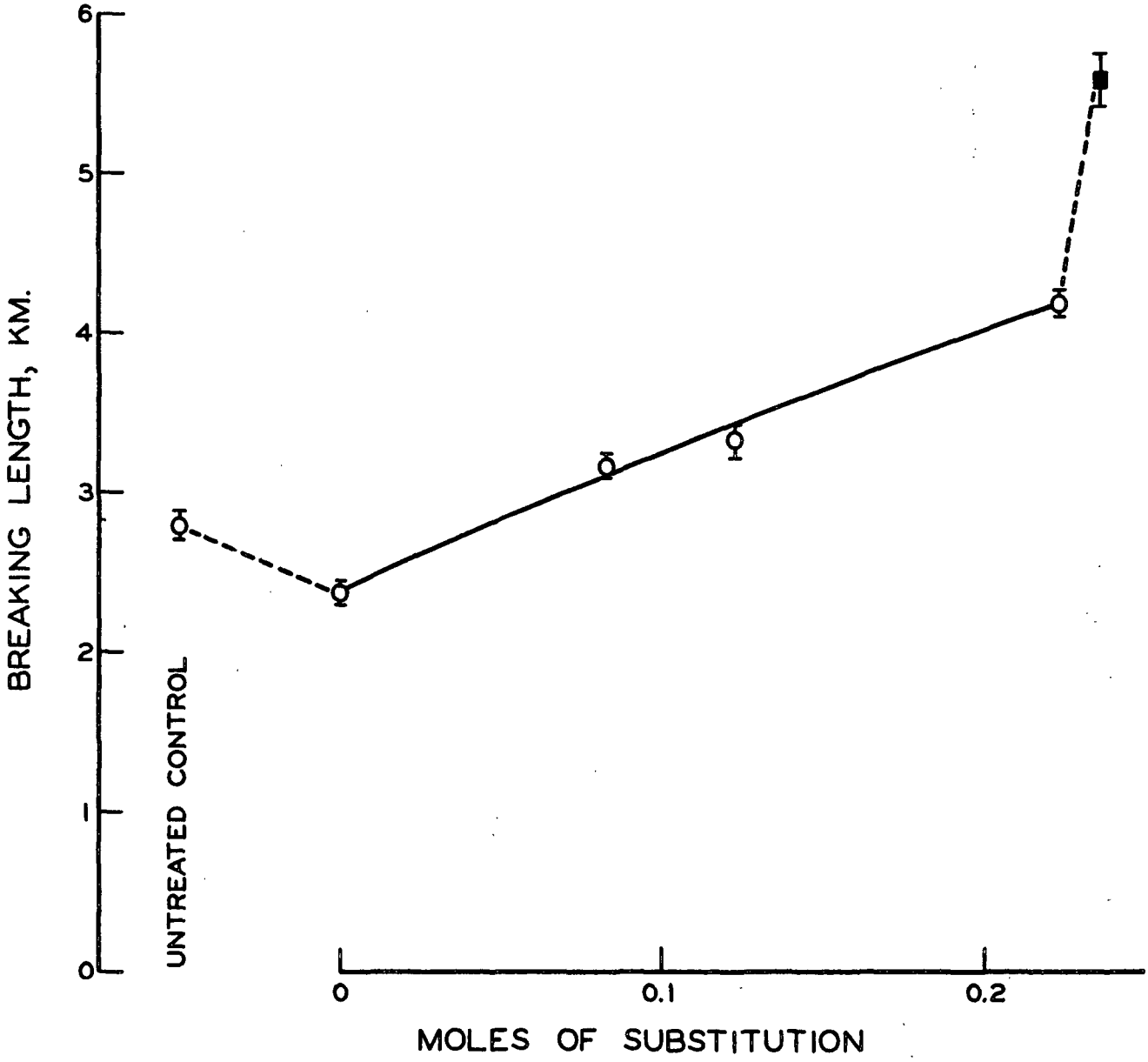

Figure 10. Effect of Hydroxyethylation on the Tensile Strength of Handsheets

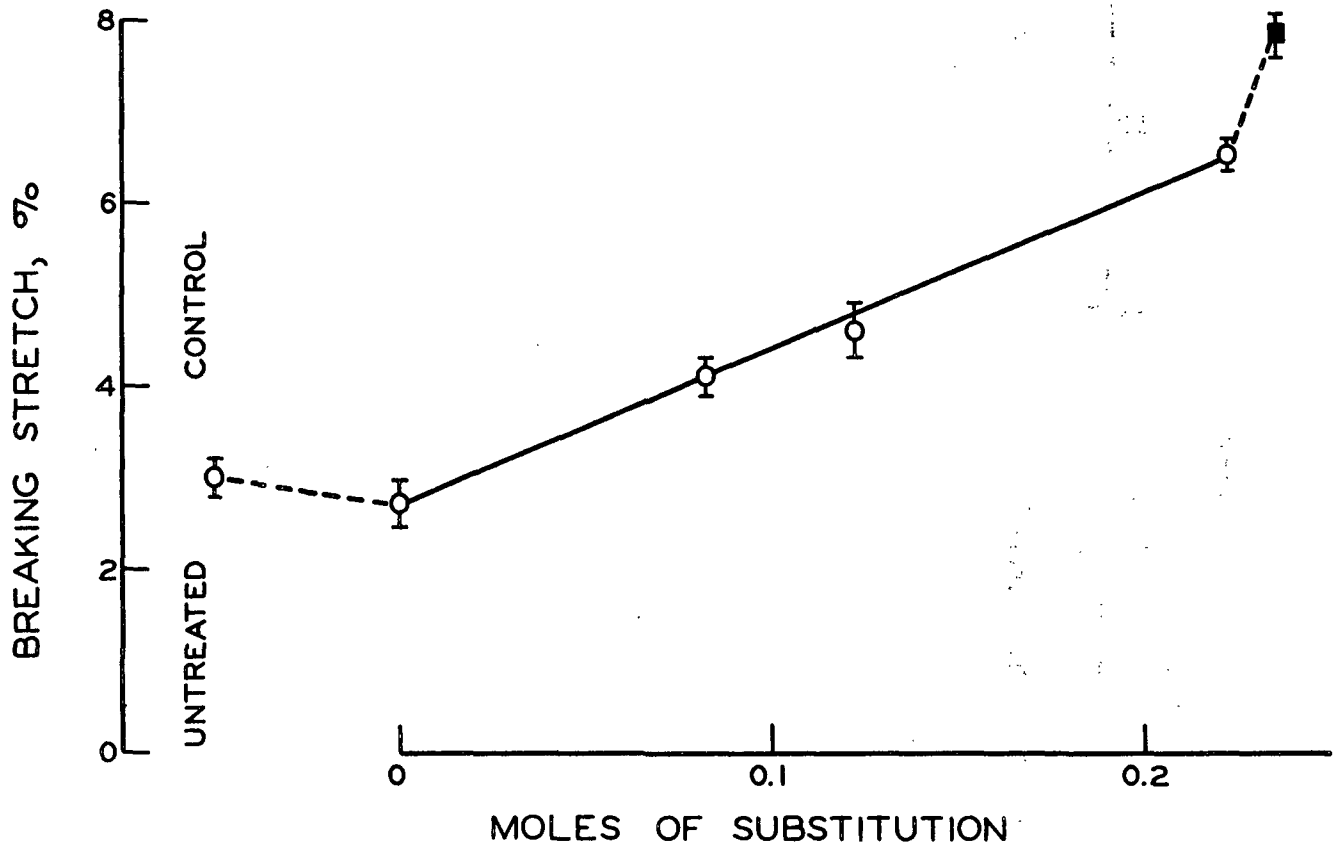

Figure 11. Effect of Hydroxyethylation on the Breaking Stretch of Handsheets

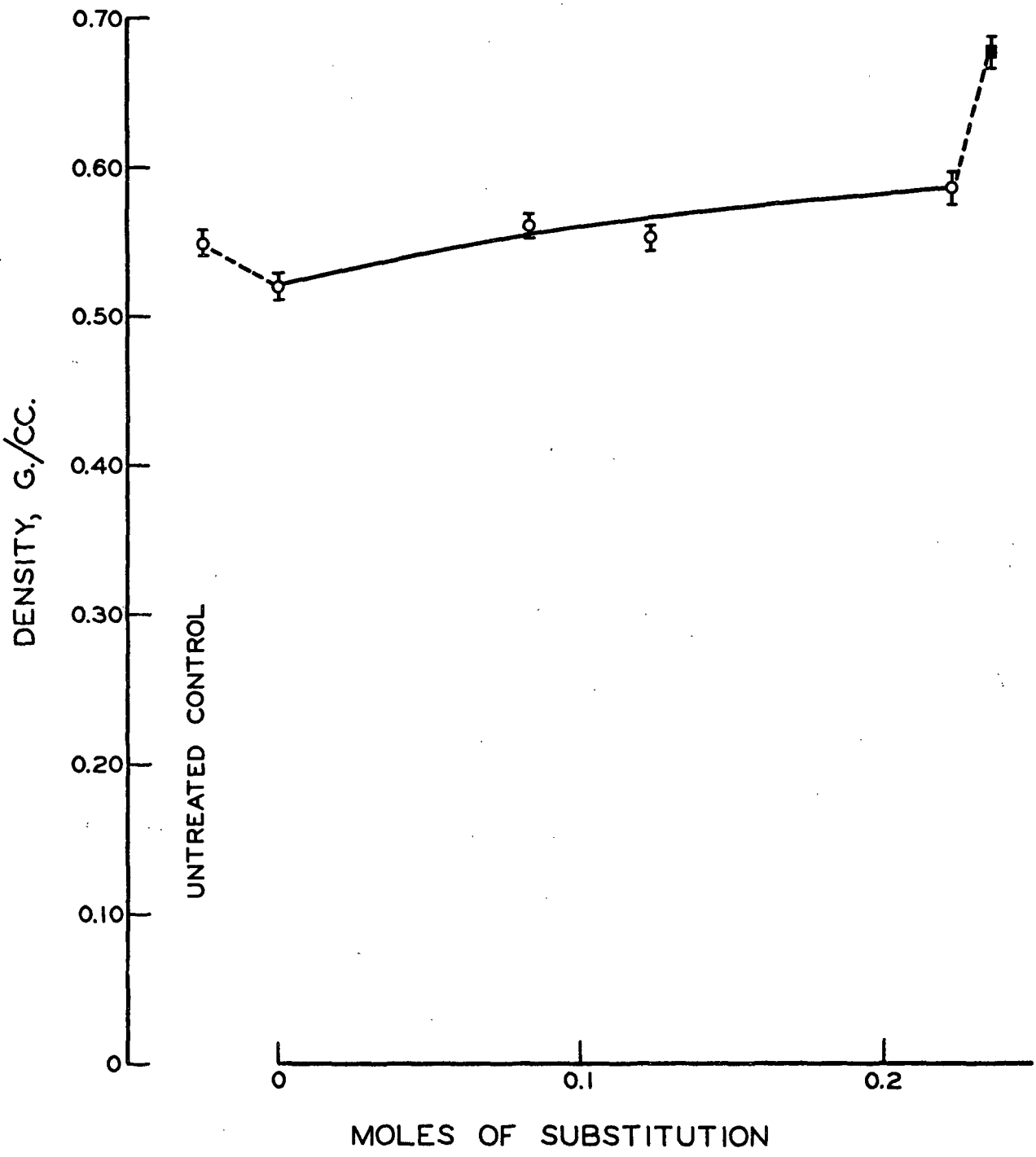

Figure 12. Effect of Hydroxyethylation on the Density of the Handsheets

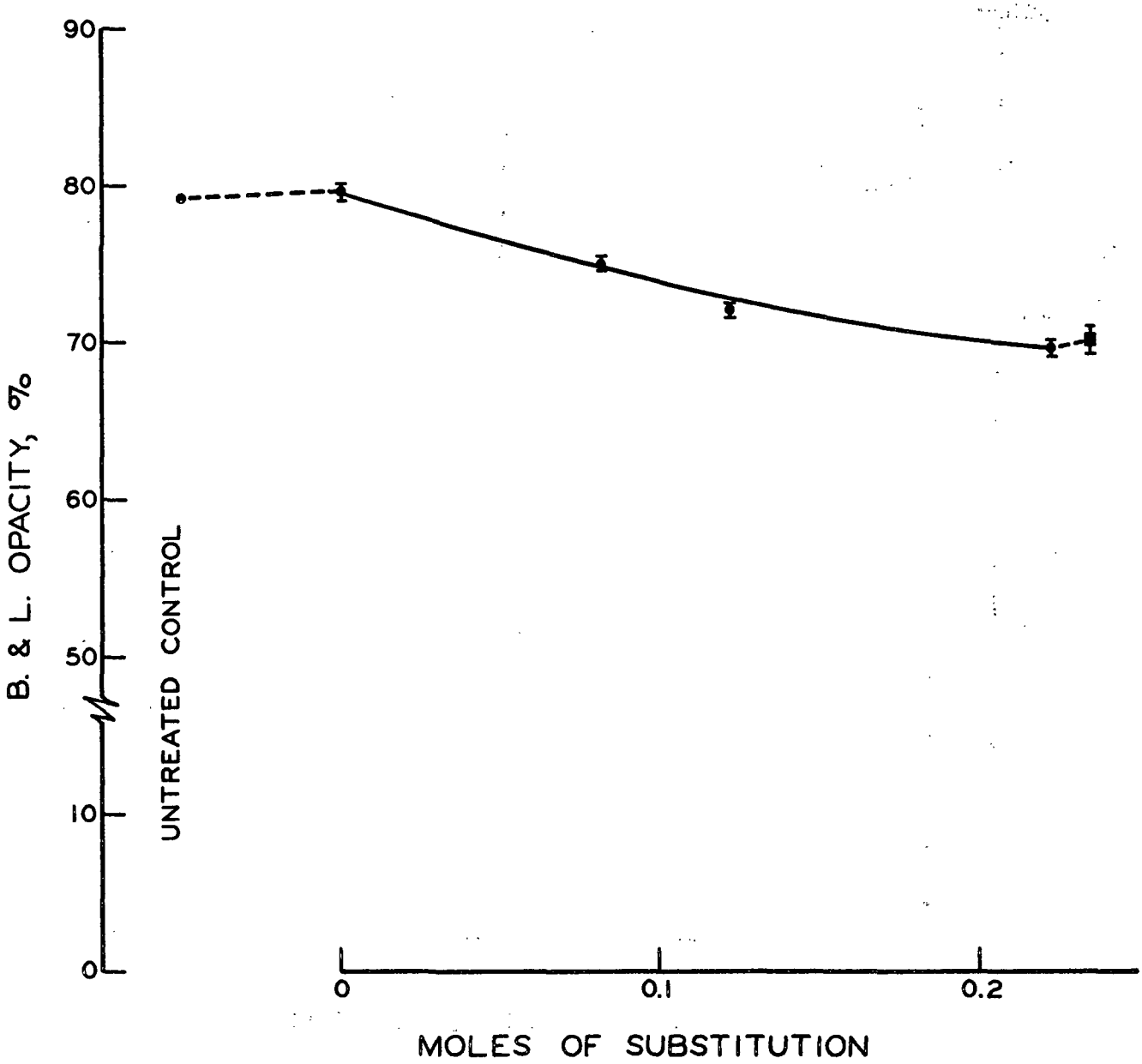

Figure 13. Effect of Hydroxyethylation on the B.&L. Opacity of the Handsheets

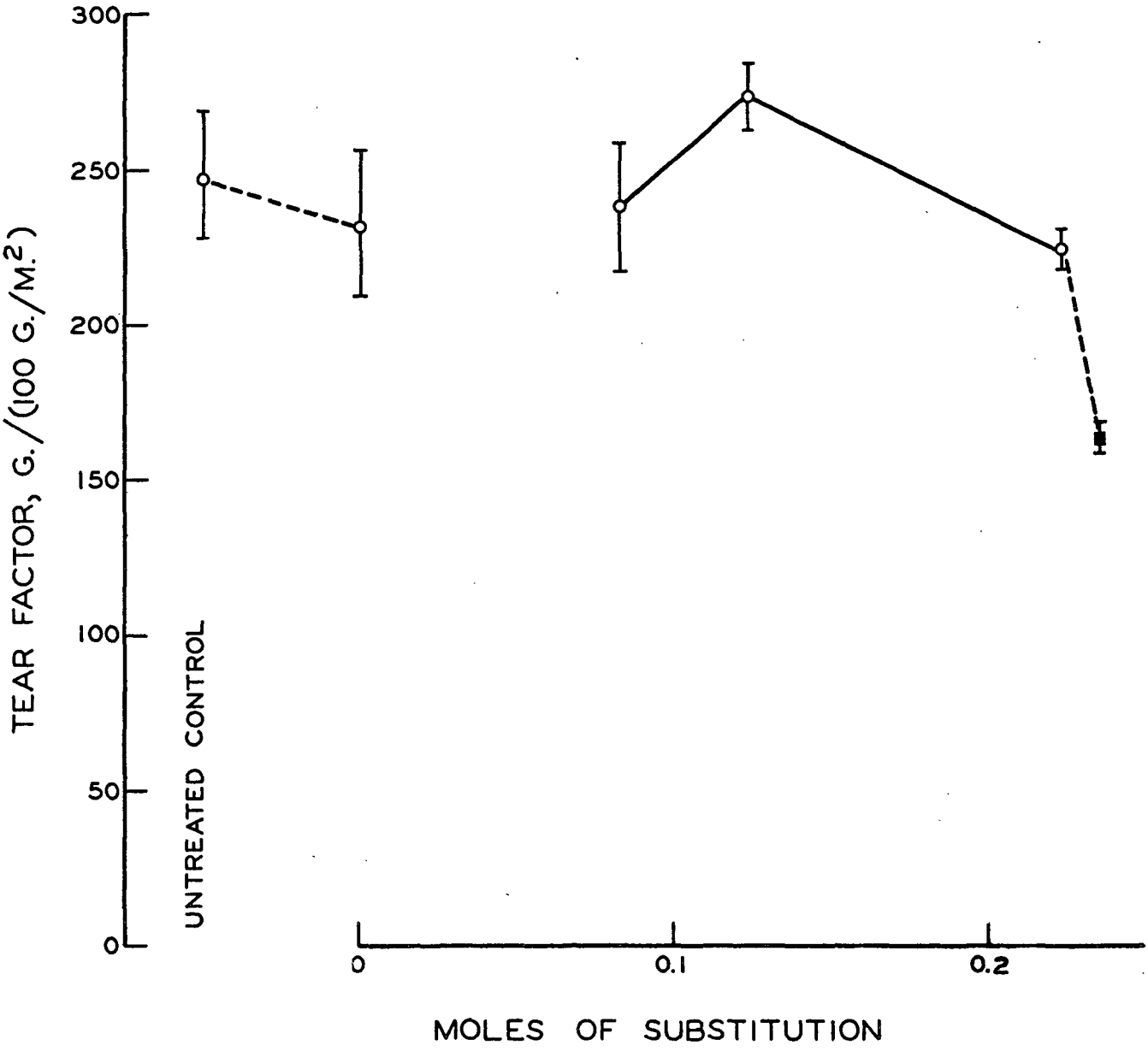

Figure 14. Effect of Hydroxyethylation on the Tearing Strength of Handsheets

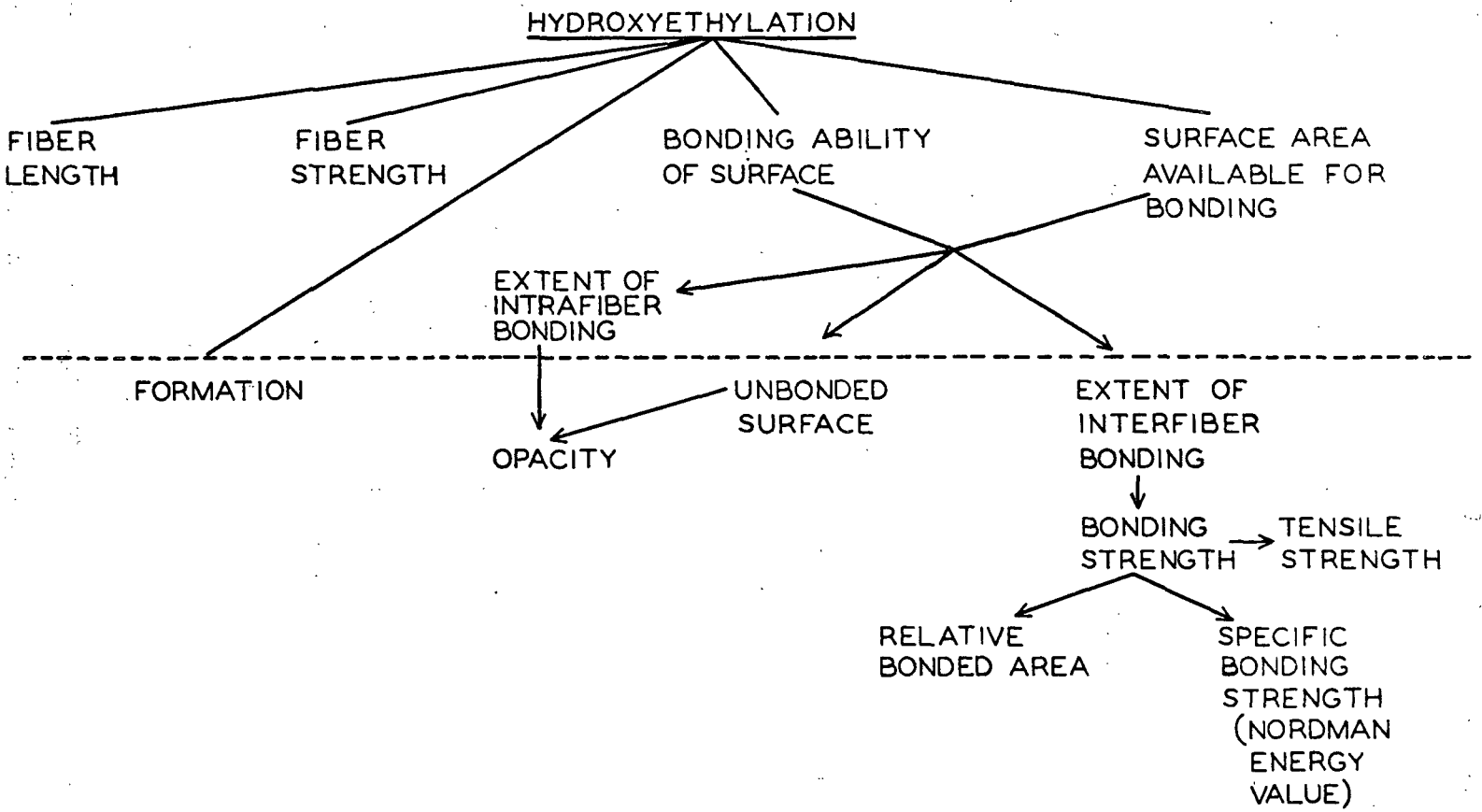

Figure 15. A Schematic Sketch of Interactions Involved in the Development of Strength of Hydroxyethylated Pulp Handsheets. Fiber Properties Above the Dotted Line and Sheet Properties Below the Dotted Line

During the treatment, the weighted average fiber lengths of the various handsheet pulps did not change enough to be significantly different from each other. This is shown by the results of the fiber length distribution in Table IV.

The formation in Thwing units of the handsheets shows a slightly decreasing trend with increasing degree of hydroxyethylation (Table V and Fig. 16). The changes in formation values are therefore not contributing to the observed increases in the strength of paper on hydroxyethylation.

The strength of the individual fibers as tested on the IPC Fiber Load-Elongation Recorder is not changed with hydroxyethylation, at the 90% confidence level (Table V). The zero-span tensile test does show a significant decrease (at the 95% confidence level) in values with hydroxyethylation, though the overall change is small (Fig. 17). These results are contrary to the zero-span values obtained by Ward (56) for hydroxyethylated cotton linters which have been subjected to beating after hydroxyethylation. The samples in the present study have not been subjected to beating after hydroxyethylation.

It is obvious that the zero-span tensile values cannot be interpreted in terms of changed individual fiber strength, at least for the unbeaten hydroxyethylated cotton fibers. A comparison of the values from the above two methods of measuring fiber strength indicate a good correlation in the untreated samples. The correlation breaks down with the alkali-treated and hydroxyethylated comber samples (Table V). The hydroxyethylated fibers, which are more deformable than the untreated ones (Table V), are liable to be deformed under the jaws during the zero-span tensile test. This may cause the values to deviate from the true fiber strength. Under any circumstances, there is no observed increase in the fiber strength values. It can be concluded that the changes in the fiber strength do not contribute to the observed increase in the strength values of the handsheets made from hydroxyethylated pulps.

TABLE IV

FIBER LENGTH DISTRIBUTION OF THE HANDSHEET PULP

Fiber Length Interval, mm.	Av. Fiber Length, mm.	Classified										Unclassified[c]	
		C-U		HE-0.0		HE-0.5		HE-1.0		HE-1.5		HE-1.5	
		A[a]	B[b]	A	B	A	B	A	B	A	B	A	B
0.1-0.3	0.2	15	1.0	16	1.1	8	0.5	4	0.3	18	1.2	17	1.2
0.3-0.5	0.4	65	4.5	72	5.0	59	4.1	57	4.0	75	5.2	80	5.5
0.5-0.7	0.6	184	12.7	196	13.5	154	10.6	138	9.6	209	14.4	228	15.7
0.7-0.9	0.8	273	18.9	294	20.3	307	21.1	264	18.4	315	21.7	311	21.5
0.9-1.1	1.0	282	19.5	249	17.2	267	18.3	217	15.1	233	16.1	213	14.7
1.1-1.3	1.2	167	11.6	171	11.8	177	12.2	154	10.7	159	11.0	152	10.5
1.3-1.5	1.4	109	7.5	112	7.7	127	8.7	127	8.8	89	6.1	115	7.9
1.5-1.7	1.6	87	6.0	68	4.7	97	6.7	94	6.5	72	5.0	73	5.0
1.7-1.9	1.8	51	3.5	64	4.4	48	3.3	98	6.8	59	4.1	56	3.9
1.9-2.1	2.0	48	3.3	47	3.2	34	2.3	70	4.9	53	3.7	38	2.6
2.1-2.3	2.2	34	2.4	39	2.7	34	2.3	54	3.8	30	2.1	43	3.0
2.3-2.5	2.4	28	1.9	23	1.6	34	2.3	42	2.9	34	2.3	37	2.6
2.5-2.7	2.6	25	1.7	13	0.9	24	1.6	34	2.4	31	2.1	13	0.9
2.7-2.9	2.8	24	1.7	29	2.0	24	1.6	24	1.7	21	1.4	17	1.2
2.9-3.1	3.0	13	0.9	15	1.0	13	0.9	13	0.9	11	0.8	10	0.7
3.1-3.3	3.2	10	0.7	10	0.7	11	0.8	13	0.9	13	0.9	9	0.6
3.3-3.5	3.4	6	0.4	7	0.5	15	1.0	5	0.3	9	0.6	6	0.4
3.5-3.7	3.6	3	0.2	5	0.3	6	0.4	4	0.3	4	0.3	7	0.5
3.7-3.9	3.8	7	0.5	5	0.3	5	0.3	8	0.6	5	0.3	9	0.6
3.9-4.1	4.0	5	0.3	4	0.3	3	0.2	4	0.3	5	0.3	4	0.3
4.1-4.3	4.2	3	0.2	4	0.3	2	0.1	4	0.3	1	0.1	1	0.1
4.3-4.5	4.4	2	0.1	1	0.1	4	0.3	4	0.3	2	0.1		
4.5-4.7	4.6	1	0.1	1	0.1	1	0.1	2	0.1	2	0.1	1	0.1
4.7-4.9	4.8	2	0.1	2	0.1	1	0.1					3	0.2
4.9-5.1	5.0			2	0.1	1	0.1	1	0.1	1	0.1	2	0.1
5.1-5.3	5.2			1	0.1			1	0.1			2	0.1
5.3-5.5	5.4							1	0.1				
5.5-5.7	5.6											1	0.1
	Total	1444	99.7	1450	100.0	1456	99.9	1437	100.2	1451	100.0	1448	100.0
Arith. av. length, mm.		1.22		1.22		1.25		1.36		1.21		1.20	
Weighted av. length, mm.		1.63		1.65		1.67		1.79		1.63		1.66	

[a] A = number of fibers.

[b] B = frequency, %.

[c] The fiber fraction below 0.1 mm. has not been measured here. Bauer-McNett classification shows: Fines (fraction through 65-, but retained on 200-mesh) – 9.4%.

TABLE V

PROPERTIES OF HANDSHEETS PREPARED FROM UNMODIFIED AND HYDROXYETHYLATED PULPS

Moles of Subs. (M.S.)	Formation Thwing Units	Fiber Strength				Initial Modulus (from Single Fiber Test), kg./mm.^{2}
		Single Fiber Test[a] Breaking Stress, kg./mm.^{2}	Zero-Span Tensile Test			
			Breaking Length, km.	Breaking[b] Stress, kg./mm.^{2}	% of Single Fiber Test	
Control	53.8±0.62[c]	70.0±7.6	16.0±0.22	66.3±0.91	95	788±114
0.000	52.6±0.61	82.2±8.6	15.9±0.23	65.9±0.95	79.5	694± 85
0.082	50.5±0.60	--	15.5±0.16	--	--	--
0.122	50.5±0.70	--	15.2±0.19	--	--	--
0.220	60.2±1.07	68.2±7.2	14.5±0.11	60.5±0.41	89	564± 60
0.232[d]	50.0±0.37	--	14.1±0.26	--	--	--

[a] Breaking stress = (av. breaking load for a batch of 27 fibers)/(av. cross-sectional area for separate batch of 27 fibers).

[b] Breaking stress, kg./mm.^{2} = (8/3) (ρ) ($\underline{B}$), where ρ = density of cellulose (1.55); and $\underline{B}$ = zero-span breaking length, km.

[c] Standard error.

[d] Unclassified sample.

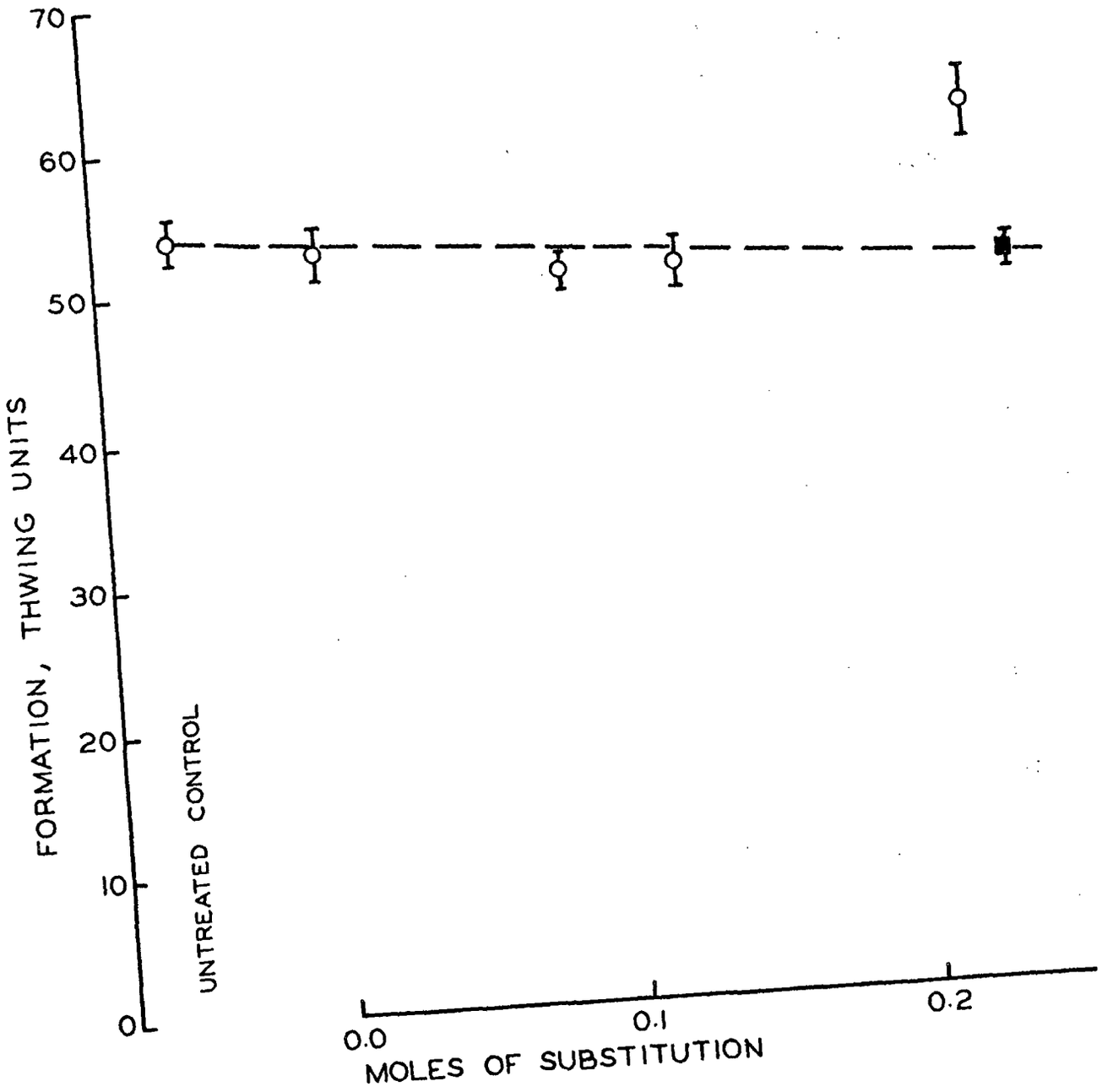

Figure 16. Effect of Hydroxyethylation on the Formation of Handsheets

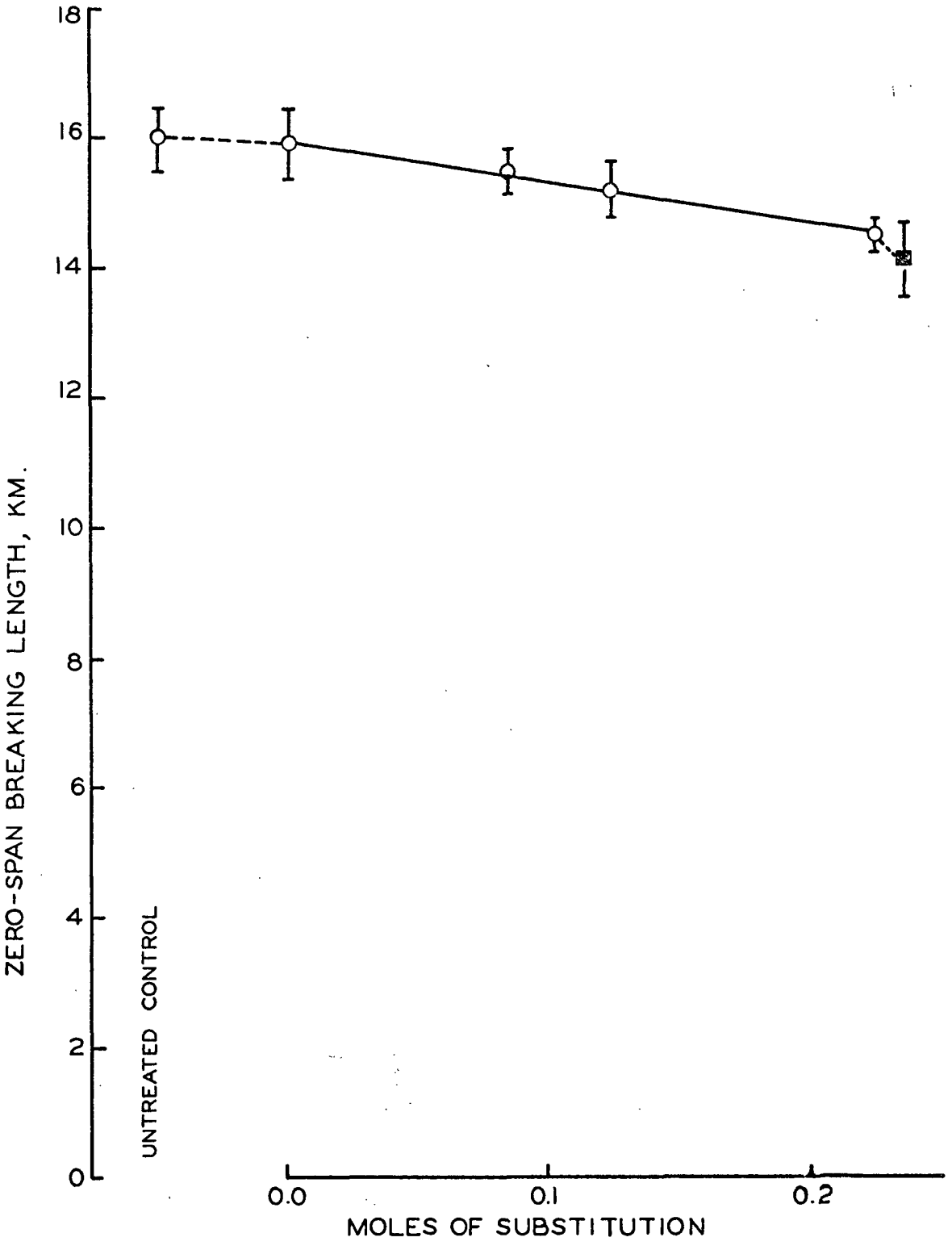

Figure 17. Effect of Hydroxyethylation on the Zero-Span Test Values of Handsheets

There is no evidence in the present study to indicate that the surface area of fibers available for bonding increases with hydroxyethylation (without beating). The hydrodynamic surface areas of the handsheet pulps (Fig. 18) and the gas sorption areas of the unbonded, water-dried fiber samples (Table VI) also decrease with increased degree of hydroxyethylation.

Thus far, the analysis has not included the effects of hydroxyethylation on bonding. Under the microscope, the fibers appear more translucent on hydroxyethylation (Fig. 19 and 20), indicating increased intrafiber bonding. The unbonded areas in the handsheets per gram of the sample also go down with increased degree of hydroxyethylation, as shown by both optical and gas sorption methods (Table VI). Consequently, the opacity of the handsheets goes down and the interfiber bonding increases as measured by both the z-direction tensile test and the IPC bonding strength test (Table VII, Fig. 21). The latter shows a good correlation with the tensile and folding endurance values of the handsheets prepared from pulps hydroxyethylated to different extents (Fig. 22).

The increase in bonding strength itself may result from two principal effects: an increase in the bonded area in relation to the total available area (referred to as relative bonded area); and also, an increase in the bonding strength within the same bonded area (referred to as specific bonding strength).

The percent relative bonded areas of the handsheets calculated from the gas sorption values of the unbonded, water-dried fibers and of the unbonded areas in the handsheets, are shown in Table VI. The alkali treatment significantly lowers the percent relative bonded area. This is not unexpected, but the magnitude of the effect here (a drop from 24.06 to 5.01) is surprising. With hydroxyethylation, the relative bonded area increases up to a point and then levels off. The maximum

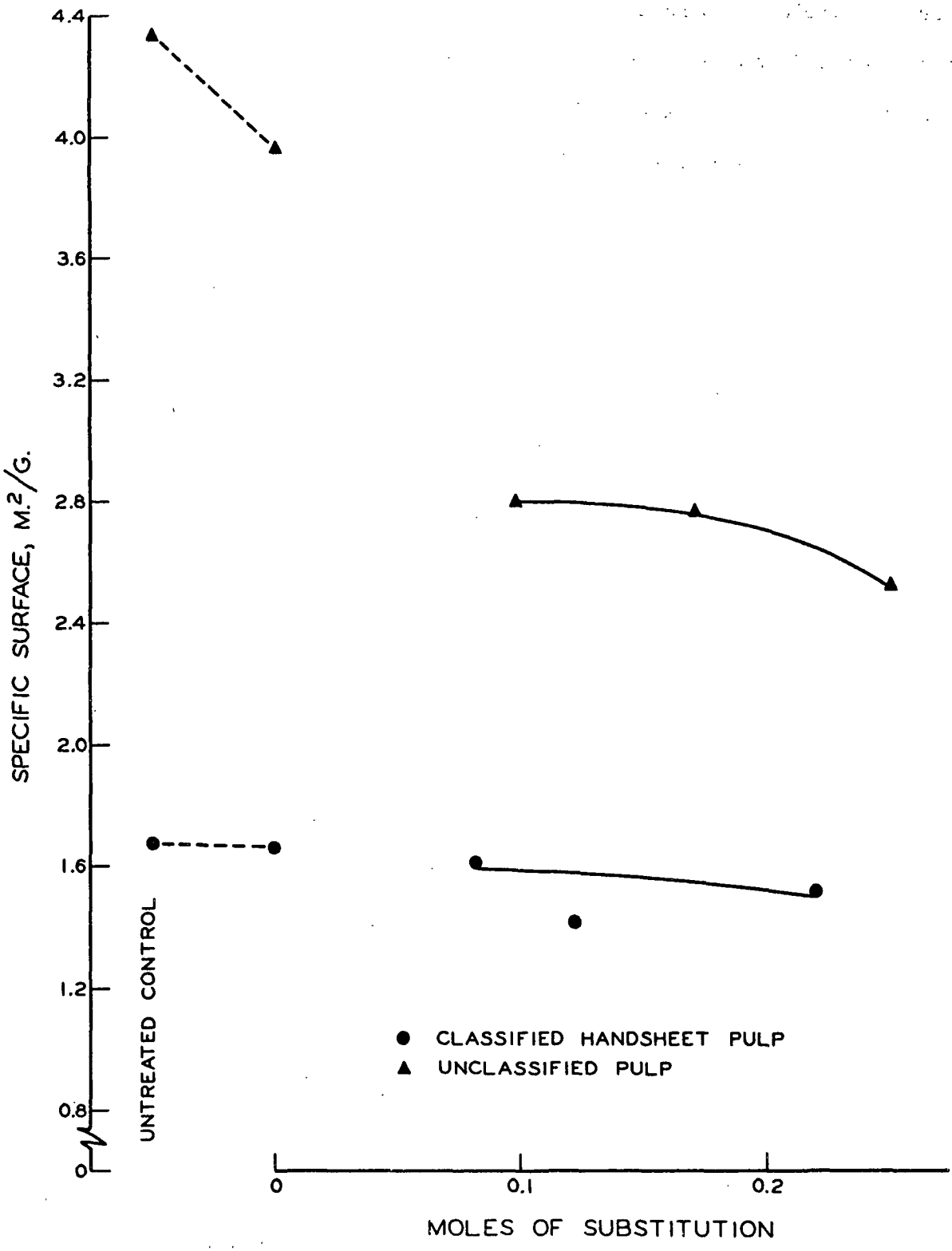

Figure 18. Moles of Substitution vs. Hydrodynamic Specific Surface of Hydroxyethylated Comber Pulps

TABLE VI

SURFACE AREAS OF HANDSHEETS PREPARED FROM UNMODIFIED AND HYDROXYETHYLATED PULPS

Moles of Subs. (M.S.)	Unbonded, Water-Dried Fibers: Gas Sorption Surface Area, $cm.^2/g. \times 10^{-4}$ (A)	Unbonded Area in Handsheet: Optical Scattering Coeff., $cm.^2/g.$ (B)	Unbonded Area in Handsheet: Gas Sorption Value $cm.^2/g. \times 10^{-4}$ (C)	Ratio = (C)/(B)	Relative Bonded Area, (Gas Sorption) % = $\frac{(A)-(C)}{(A)} \times 100$
Control	1.226±0.043	365±1.0	0.931±0.0265	25.5	24.06
0.000	1.017±0.033	367±1.3	0.966±0.0165	26.3	5.01
0.082	0.833±0.013	311±0.8	0.656±0.0150	21.1	21.25
0.122	0.857±0.014	281±1.2	0.566±0.0110	20.1	33.96
0.220	0.745±0.018	261±0.7	0.506±0.0150	19.4	32.08

Gas sorption values: each value mean of 6-8 sorption measurements.

Optical scattering coeff.: each value mean of at least 12 measurements.

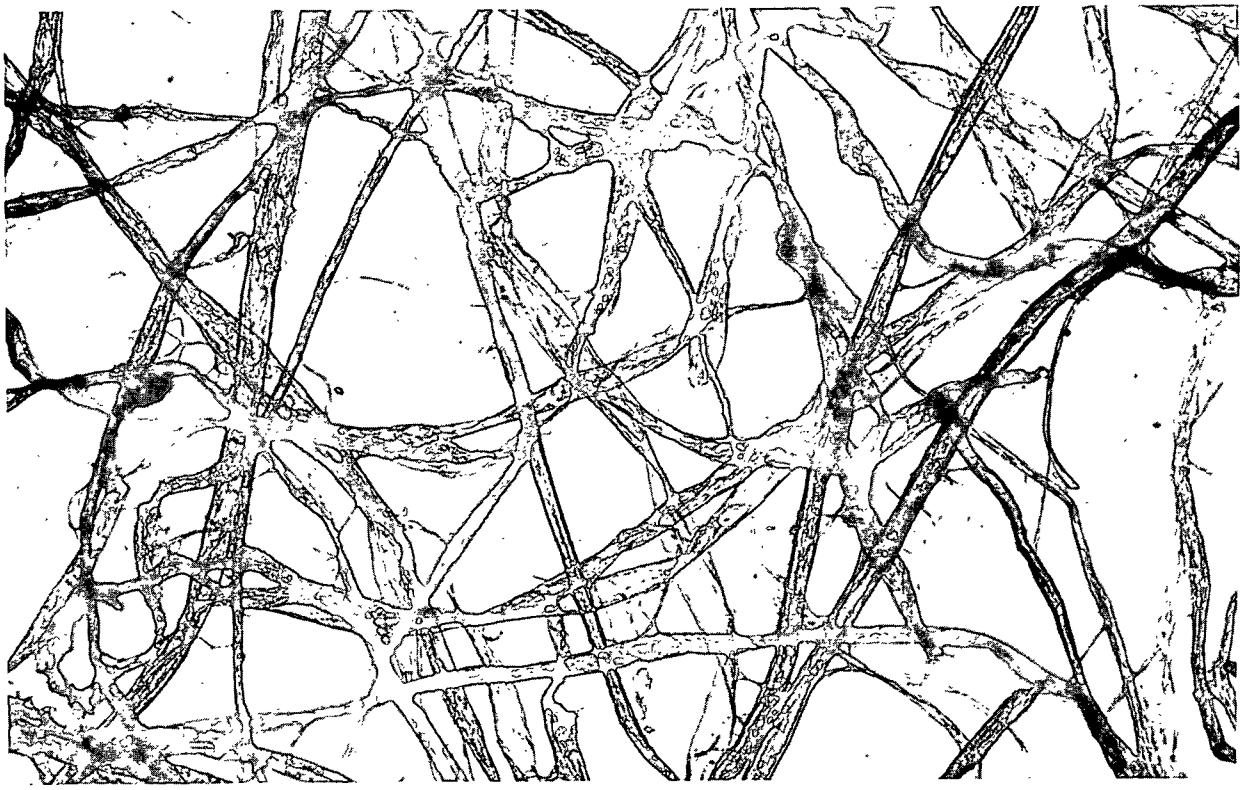

Figure 19. Sample M.S. = 0.0 in Dry Mounting, Bright Field Illumination at 185X

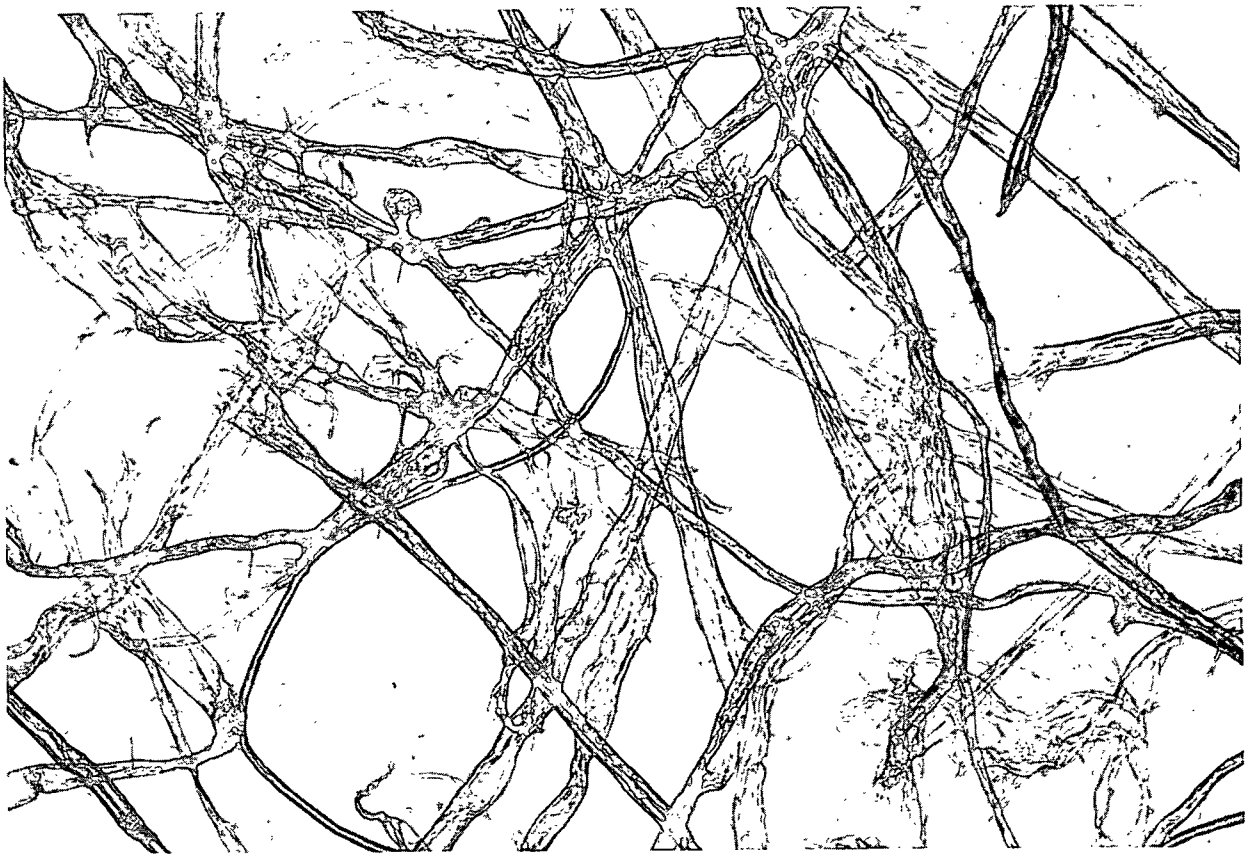

Figure 20. Sample M.S. = 0.22 in Dry Mounting, Bright Field Illumination at 185X

TABLE VII

BONDING STRENGTH OF HANDSHEETS PREPARED FROM UNMODIFIED AND HYDROXYETHYLATED PULPS

Moles of Subs. (M.S.)	z-Direction Tensile[a], kg./cm.^{2}	IPC Bonding Strength[a] (VVP), kp.-cm./sec.	Intrinsic Bonding Strength, kp.-cm./sec.	Nordman Bonding Strength[b], kg.cm./cm.^{2}	
				Optical Scattering Method	Gas Sorption Method
Control	3.66±0.045	<0.5	2.08×10^{-2}	0.125±0.0049[c]	0.00414±0.000509[c]
0.000	2.98±0.046	<0.5	--	0.141±0.0451	0.00428±0.000297
0.082	4.66±0.082	1.47±0.060	6.92×10^{-2}	0.222±0.0232	0.00705±0.002450
0.122	4.89±0.062	2.60±0.043	7.66×10^{-2}	0.261±0.0370	0.00825±0.002120
0.220	6.04±0.155	5.33±0.256	16.61×10^{-2}	0.357±0.0957	0.00842±0.000081
0.232[d]	--	29.60±1.410	--	0.408±0.0676	0.01103±0.000572

[a] Mean value of five measurements.

[b] Calculated from the linear regression analysis as average slope = $(b_x + 1/b_y)/2$, where b_x refers to regression coefficient when the change in surface area is the independent variable (x).

[c] Standard error for b_x only. Observation points--3.

[d] Unclassified sample.

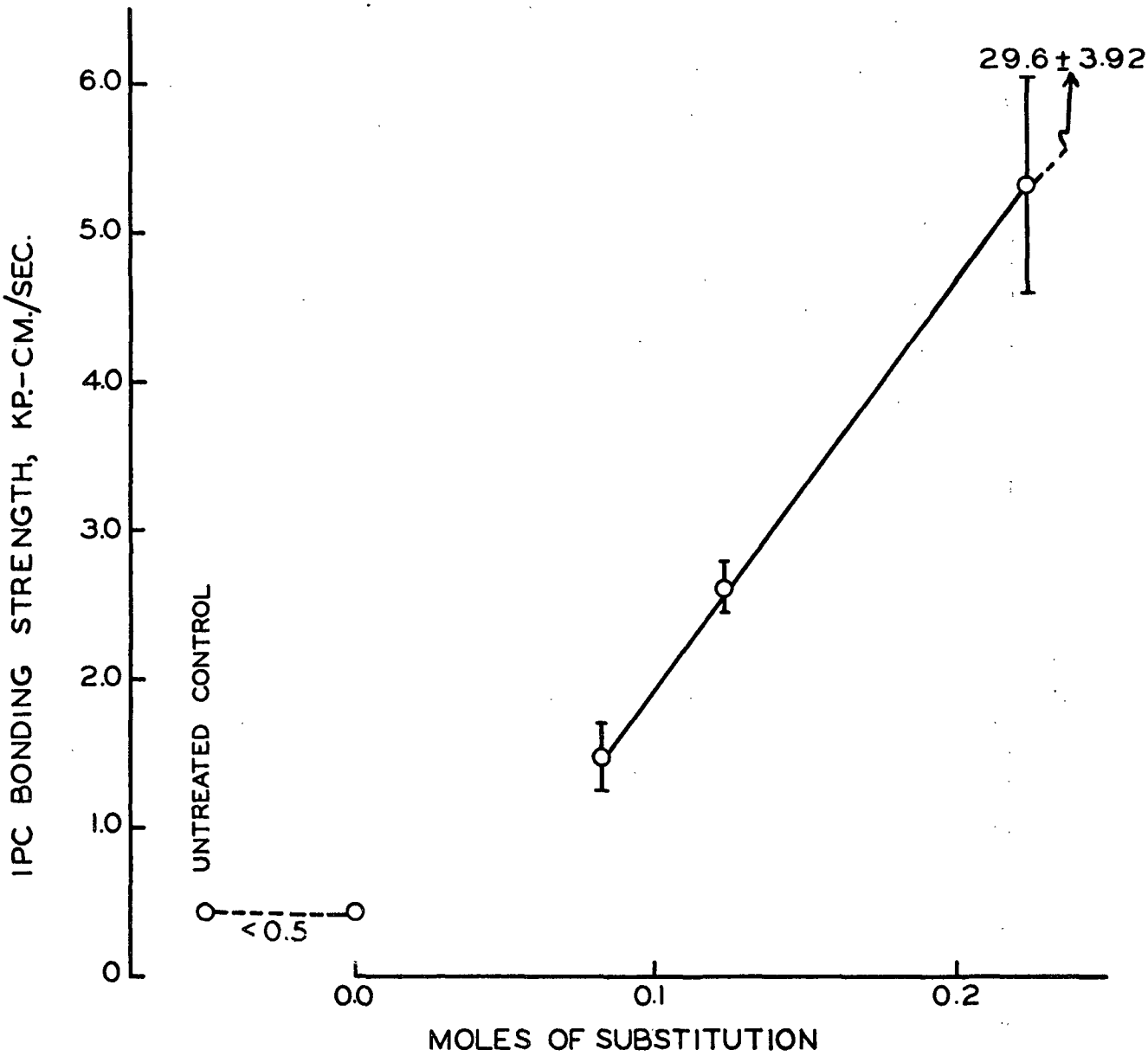

Figure 21. Effect of Hydroxyethylation on the IPC Bonding Strength of Handsheets

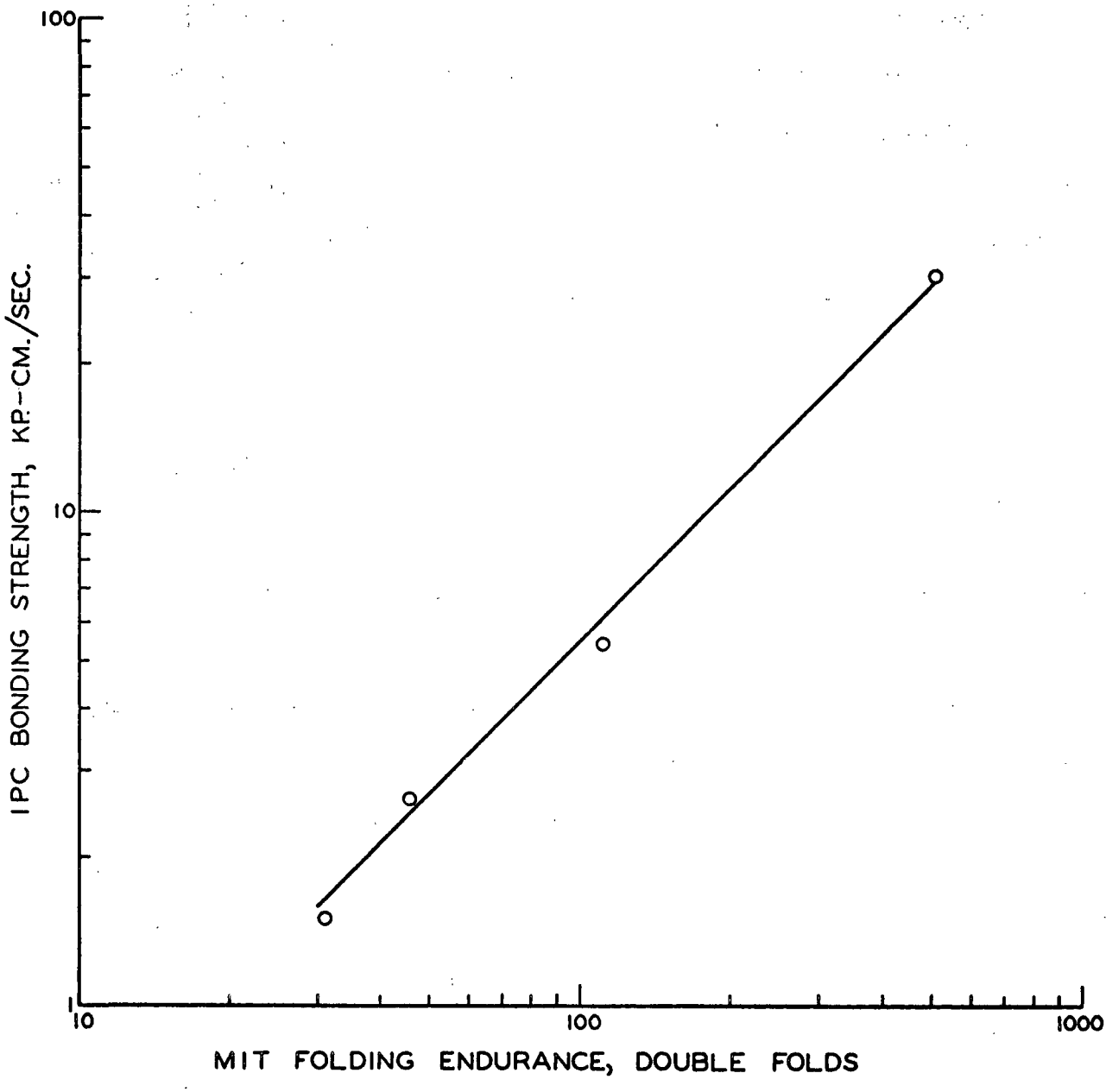

Figure 22. IPC Bonding Strength and Folding Endurance Characteristics of Comber Pulp with Moles of Substitution from 0.082 to 0.232

increase in the relative bonded area, in the present study, is about 40% of the value of the untreated control.

The specific bonding strength, obtained by division of the IPC bonding strength value by the percent relative bonded area, shows a continual increase with increased degree of hydroxyethylation (Fig. 23). The maximum increase in the specific bonding strength value on hydroxyethylation is around 700% of the value of the untreated control (Table VII). The z-direction tensile test values were not used as the irregularities of this test have been experimentally confirmed by the recent work of Wink, et al. (52). Moreover, this test is done on differently prepared handsheets, with basis weights twice the weight of the standard sheets.

The Nordman bonding strength values of the samples are given in Table VII. The hydroxyethylation treatment increases the optically determined Nordman bonding strength values, the maximum increase being around 185%. The highly substituted fines contribute another 40% increase. When confidence limits are brought into play, a significant difference at the 90% level is observed in most samples. The effect therefore appears to be real. In the case of gas sorption strength values, too, the hydroxyethylation effect increases, the maximum increase being around 100%. The presence of fines adds another 65% increase. Even though standard errors are high in some samples and the differences in values not significant at the 90% confidence level, the overall effect in this case also appears to be real. The Nordman values obtained here are in the range of 1.20×10^5 - 4.10×10^5 ergs/cm.^{2} for the optical method and 0.04×10^5 - 0.10×10^5 ergs/cm.^{2} for the gas sorption method. [The optically determined bonding strength values reported vary for wood fibers in the range of 1.6×10^5 - 8.2×10^5 ergs/cm.^{2} (37).] The ratio of optical bonding strength value to gas sorption bonding strength value ranges here from 30 to 40. This compares well with the reported value of 30 to 50 (57).

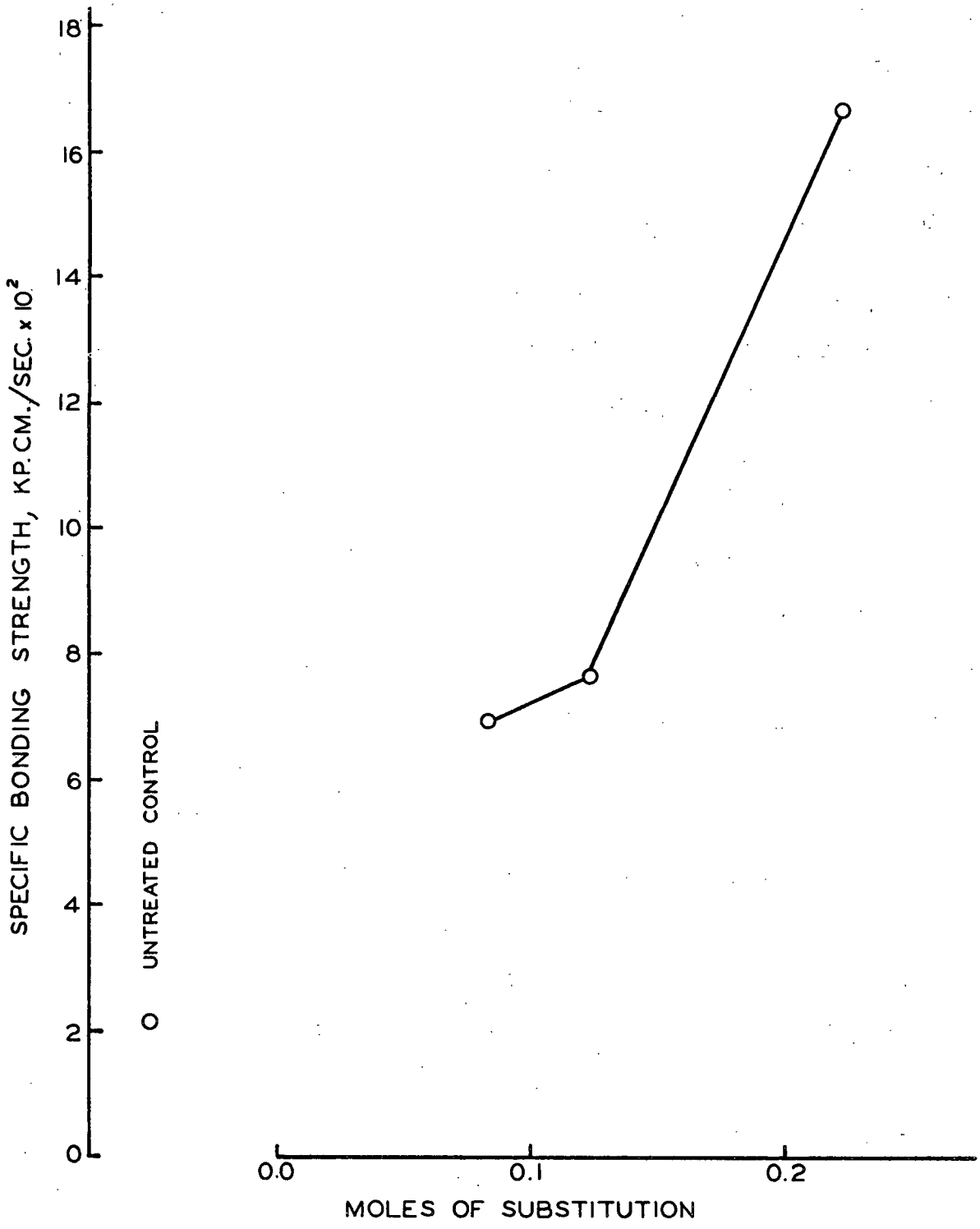

Figure 23. Effect of Hydroxyethylation on the Specific Bonding Strength of Handsheets

The above considerations show that increase in fiber-fiber bonding is almost entirely responsible for the observed increase in the strength of the hydroxyethylated pulp handsheets. Based on their maximum effects, the relative bonded area increase contributes less than 10% and the specific bonding strength increase contributes more than 90% to increased fiber-fiber bonding. The mechanism by which this is achieved can be due to increased response to the Campbell effect resulting from the hydroxyethylation of fibers.

Hydrodynamic properties of the handsheet pulps as well as of the whole (not classified) pulps are shown in Tables VIII and IX. A continual increase in the compressibility constant, $\underline{M}$, on hydroxyethylation is obtained (Fig. 24). A slight decrease in hydrodynamic specific surface, $\underline{S}_w$, (Fig. 18) and an abrupt decrease in specific volume, $\underline{V}$, (Fig. 25), are also observed on treatment with ethylene oxide. In the hydrodynamic sense, the swollen specific volume means the volume denied to flow and the specific surface means the surface over which water does flow. The swollen specific volume would depend on how the fibers hold water. As well as the present concepts are understood, the generalized picture is something like that given in Fig. 26. It may be seen that the increased deformability of the fibers and fibrils on hydroxyethylation can account for the observed decreases in the values of the specific surface area and swollen specific volume. In view of the lower surface area and lower specific volume, one would expect the compressibility of the mat to be a factor in the development of strength in a sheet. The relationship between compressibility constant, $\underline{M}$, and breaking length is shown in Fig. 27. Similar relationships given in Fig. 28 strongly support the importance of compressibility as a factor. Compressibility is a static test – pressure is applied to the bed. The hydrodynamic test is a nonstatic test – there is a flow of water through the bed. In hydroxyethylated fibers, both need to be considered. Effects on compressibility appear to be a major factor.

TABLE VIII

HYDRODYNAMIC PROPERTIES OF HANDSHEET PULPS

I. FILTRATION RESISTANCE DATA

ΔP, cm. of water	Filtration Resistance, $R \times 10^{-8}$ cm./g. M.S.					
	Control	0.00	0.082	0.122	0.220	0.232
10	1.11	1.12	1.28	1.14	1.47	3.88
20	1.56	1.58	1.83	1.59	2.12	6.15
30	1.94	1.98	2.27	1.96	2.65	8.12
40	2.27	2.32	2.65	2.28	3.14	10.00
50	2.60	2.64	3.01	2.60	3.60	11.70
60	2.90	2.96	3.36	2.89	4.02	13.30
70	3.19	3.27	3.69	3.19	4.42	15.00
80	3.46	3.55	4.00	3.45	4.79	16.50
90	3.71	3.82	4.29	3.70	5.16	18.00

II. COMPRESSIBILITY DATA

First Compression: $\underline{M}$, (g./cc.)/(dynes/cm.^{2})$^{\underline{N}}$
$\underline{N}$, dimensionless

Hydrodynamic Prop.: $\underline{v}$, cc./g.
$\underline{S_w}$, cm.^{2}/g.

Pressure Range: 10-100 cm. of water

Sample, M.S.	$\underline{M}$	$\underline{N}$	$\underline{S_w} \times 10^{-3}$	$\underline{v}$
Control	0.00198	0.383	16.7	2.63
0.000	0.00201	0.383	16.6	2.66
0.082	0.00279	0.369	16.1	2.06
0.122	0.00340	0.359	14.1	1.95
0.220	0.00455	0.339	15.2	1.90
0.232	0.00567	0.322	25.0	2.10

[a]Unclassified pulp.

TABLE IX

HYDRODYNAMIC PROPERTIES OF WHOLE PULPS

I. FILTRATION RESISTANCE DATA

ΔP, cm. of water	Filtration Resistance, $R \times 10^{-8}$ cm./g.				
	M.S.				
	Control	0.00	0.098	0.170	0.252
10	6.1	4.8	3.4	3.8	4.3
20	9.8	7.7	5.5	6.2	6.9
30	14.1	10.3	7.3	8.3	9.2
40	16.1	12.7	9.1	10.2	11.4
50	19.9	14.9	10.7	12.2	13.4
60	21.7	17.0	12.3	14.0	15.5
70	24.3	19.0	13.8	15.8	17.5
80	26.7	21.1	15.3	17.6	19.4
90	29.0	22.9	16.8	19.1	21.3

II. COMPRESSIBILITY DATA

First Compression: M, $(g./cc.)/(dynes/cm.^2)^N$
N, dimensionless

Hydrodynamic Prop.: v, cc./g.
S_w, $cm.^2/g.$

Pressure Range: 10-100 cm. of water

Sample, M.S.	M	N	$S_w \times 10^{-3}$	v
Control	0.00178	0.390	43.4	3.03
0.000	0.00178	0.390	39.7	3.09
0.098	0.00291	0.364	28.0	2.62
0.170	0.00360	0.351	27.7	2.48
0.252	0.00570	0.327	25.3	2.43

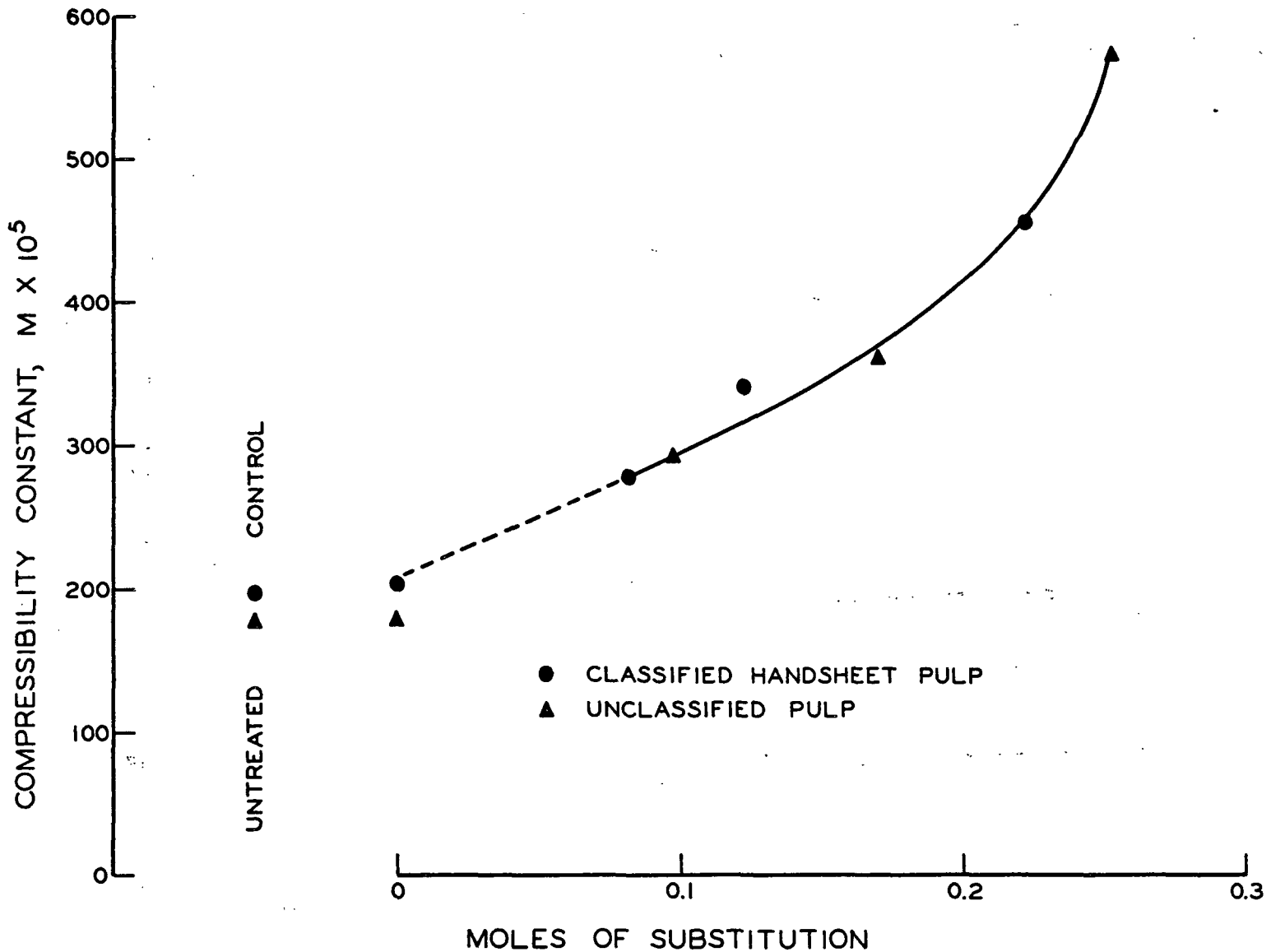

Figure 24. Moles of Substitution vs. Compressibility Constant, M, of Hydroxyethylated Comber Pulps

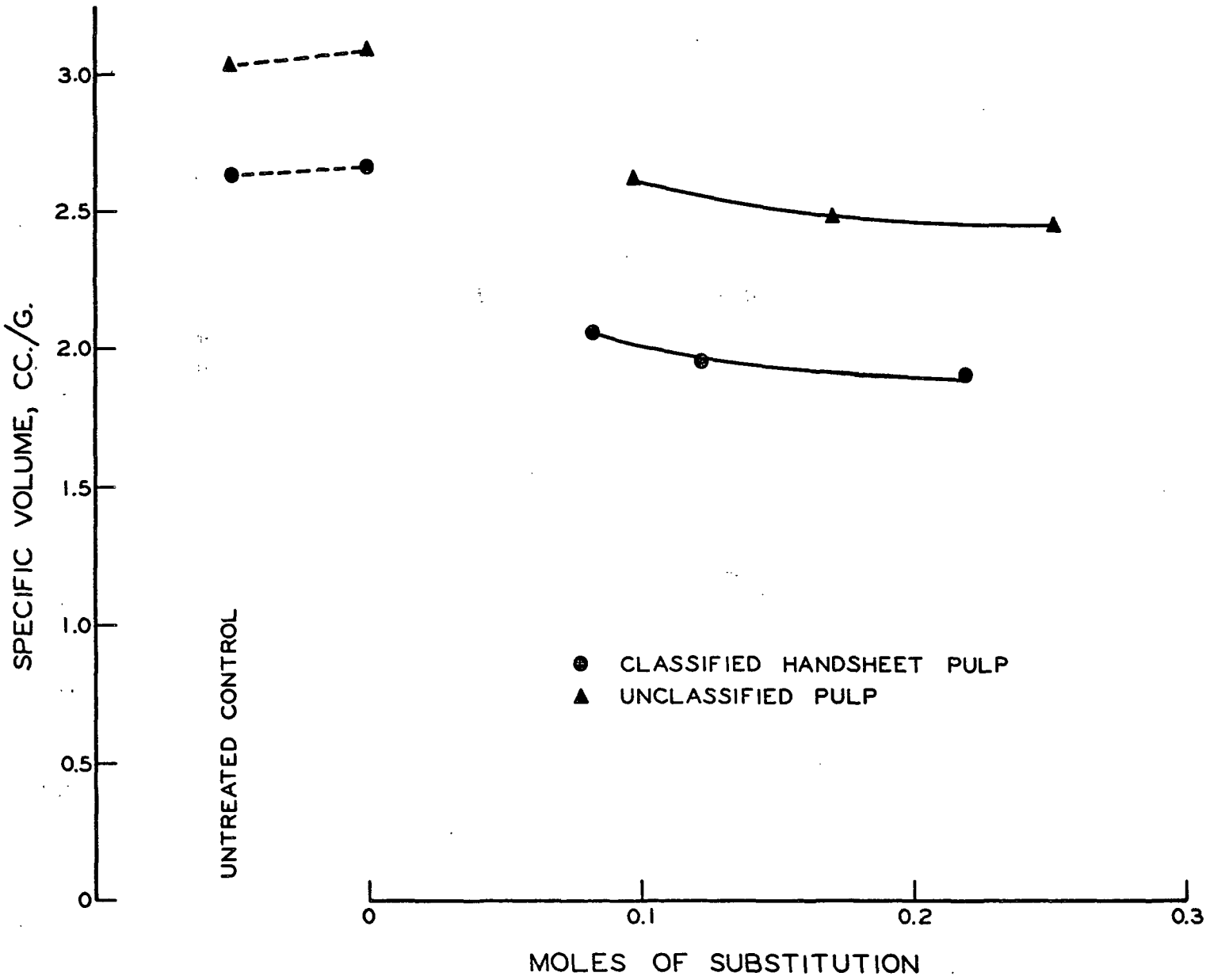

Figure 25. Moles of Substitution vs. Hydrodynamic Specific Volume of Hydroxyethylated Comber Pulps

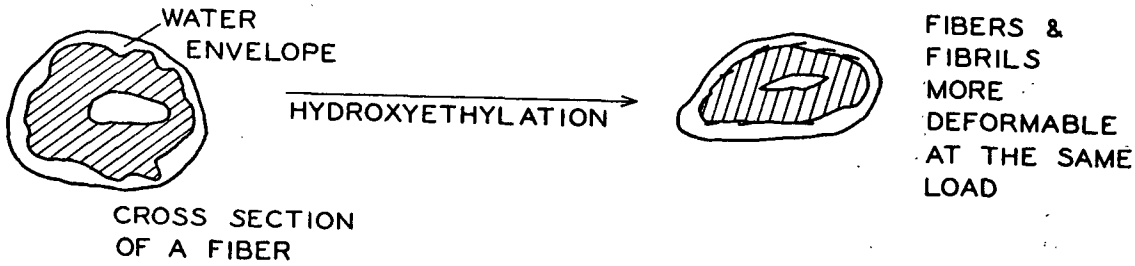

Figure 26. Generalized Picture to Explain the Decrease in Hydrodynamic Surface Area, S_w, and Volume, V

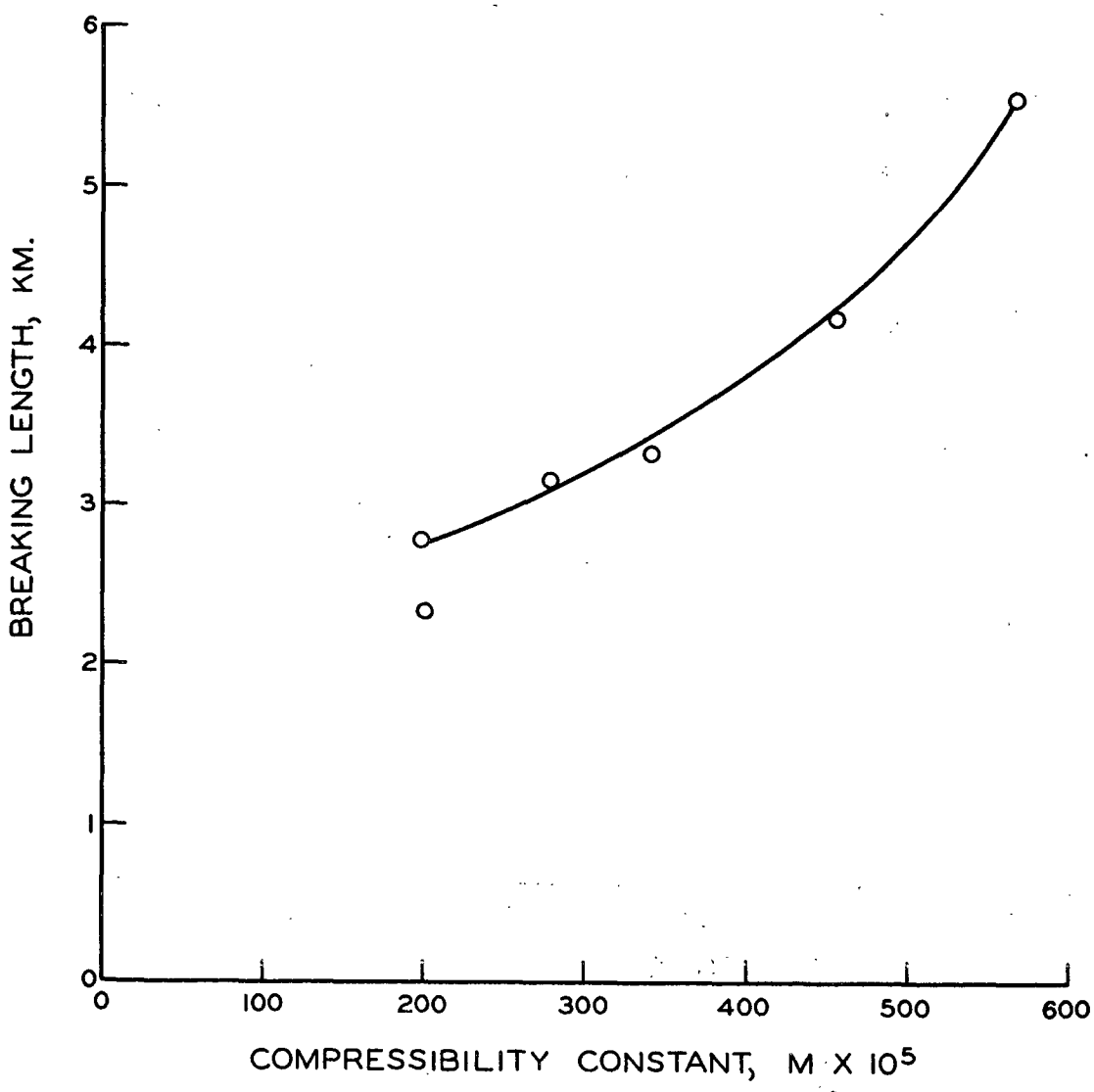

Figure 27. Compressibility Constant, M, vs. Tensile Strength of Handsheets

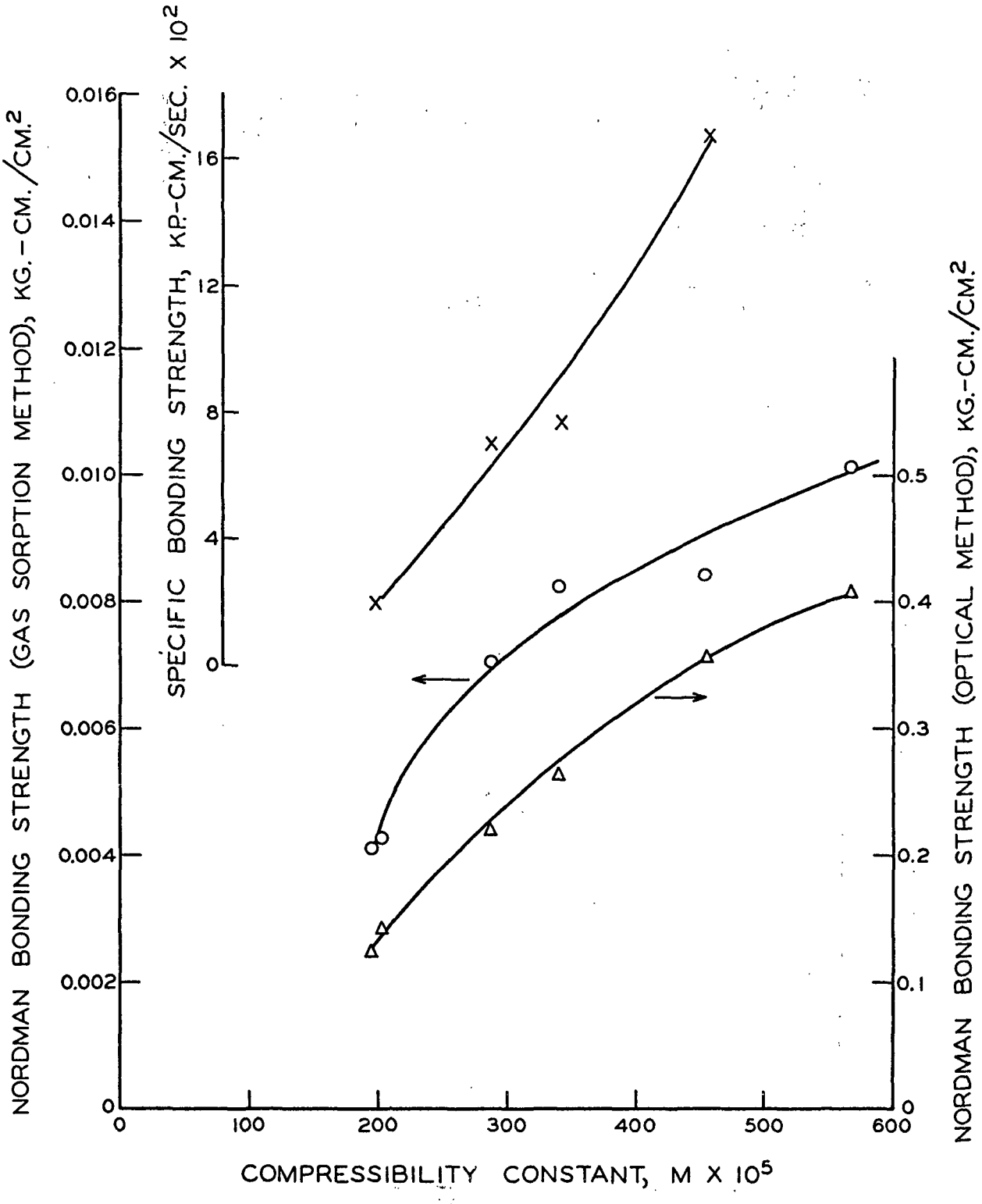

Figure 28. Compressibility Constant, M, vs. Bonding Strength Values

A fiber mat formed by the filtration of a dilute slurry possesses a highly anisotropic and porous structure. The fibers are randomly oriented in the horizontal plane with their axes generally perpendicular to the vertical direction. The essential feature of the fibrous structure is its large number of fiber-fiber contacts. When the mat is subjected to compaction, it is conceivable that the number of contacts, real or apparent, may increase by virtue of fiber bending. This increase will be greater as the fiber becomes more flexible. Also, one fiber may reposition itself with respect to another as a result of relative movement. Furthermore, the contact surfaces may conform to each other under compression.

Compressibility represents the volume change of a system under compressive stresses. The apparent factors involved in the compressibility of a fiber mat include fiber dimensions (length and diameter), fiber properties (density and modulus of elasticity), and initial structure. If the fiber dimensions and initial structure do not change significantly with the chemical treatment, then the compressibility constant, M, is approximately proportional to the inverse Nth power of the modulus of elasticity, E, (58) where N is the compressibility power as shown in Equation (4).

The modulus of elasticity of the wet fibers is not known. It is usually much lower in the wet state than in the dry state. The initial modulus of dry fibers (Table V) does decrease on hydroxyethylation (significant at the 90% confidence level), though not enough to explain the substantial increase in M. M also includes the effects of conformability and plasticity of the fibers. The modulus of elasticity gives the bending effect but before this can be effective there should be contact and this is produced by the plasticity of the fibers. In hydroxyethylated fibers, plasticity seems to be more important than elasticity. Hydroxyethylation, so to speak, provides a "built-in plasticizer" in the fibers.

The fibers actually become more viscoelastic. Fiber slippage is not likely to occur under these conditions. As soon as the load is applied, there is much contact area developed because of the increased deformability of the fibers under the pressure of contact. This will stop any slippage that might otherwise occur. The contact area enlarges as the fibers become more flattened upon increased loading, thus providing better molecular contact. Fiber conformation at the contact surfaces reduces the thickness of a fiber 'layer,' resulting in a more compacted structure.

Observations under the electron microscope support the above contention. The following observations are based on the examination of a very small area of the sample but within this limitation they are representative. The untreated and the alkali-treated handsheets show a nonconformable structure with the aggregation of microfibrils in the secondary wall intact (Fig. 29 and 30). The hydroxyethylated handsheet, on the contrary, shows a more conformable structure with smoother surface (Fig. 31). The surfaces of the fibers in this case appear to be of granular type and the aggregation of microfibrils are not so distinct (Fig. 32).

Not only the density of the handsheets increases with hydroxyethylation, but also the porosity and the average pore size (Table X). The porosity was measured, using the Bendtsen Porosimeter, and the average pore size, using the mercury intrusion method. The results suggest a high shrinkage potential and collapsing tendency of the fibers and fibrils on hydroxyethylation. This is also supported by observations under the microscope of the mercury-intruded samples. The untreated control as well as the alkali-treated sample have a considerably larger number of fibers with lumens filled with mercury than the hydroxyethylated sample (Fig. 33 and 34).

A comparison of hydroxyethylated samples with and without fines (fraction through 65- but retained on 200-mesh) shows the effect of fines. There is observed

Figure 29. Electron Micrograph of Handsheet M.S. = 0.0 (30,000X)

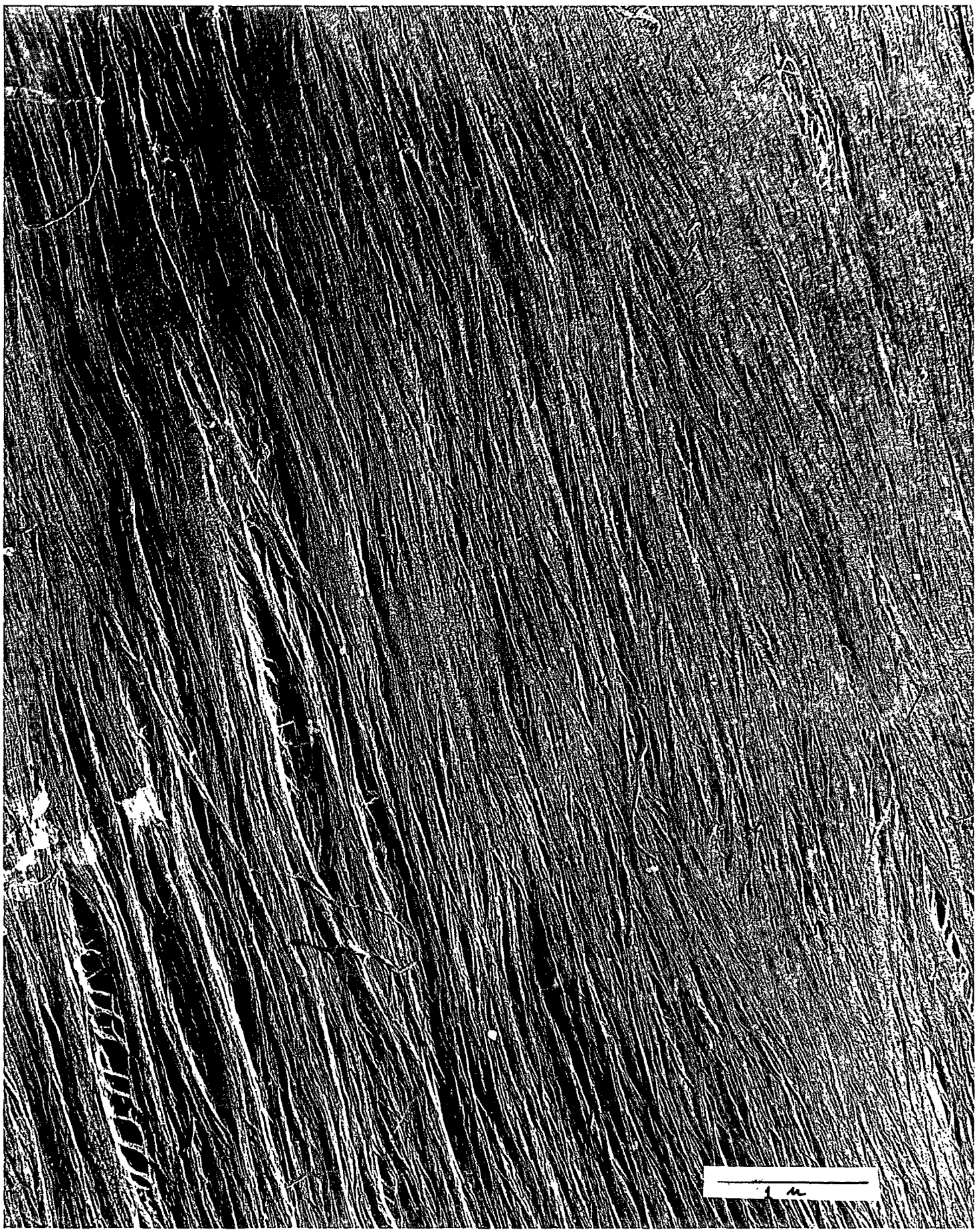

Figure 30. Electron Micrograph of Freeze-Dried Untreated Fiber (30,000X)

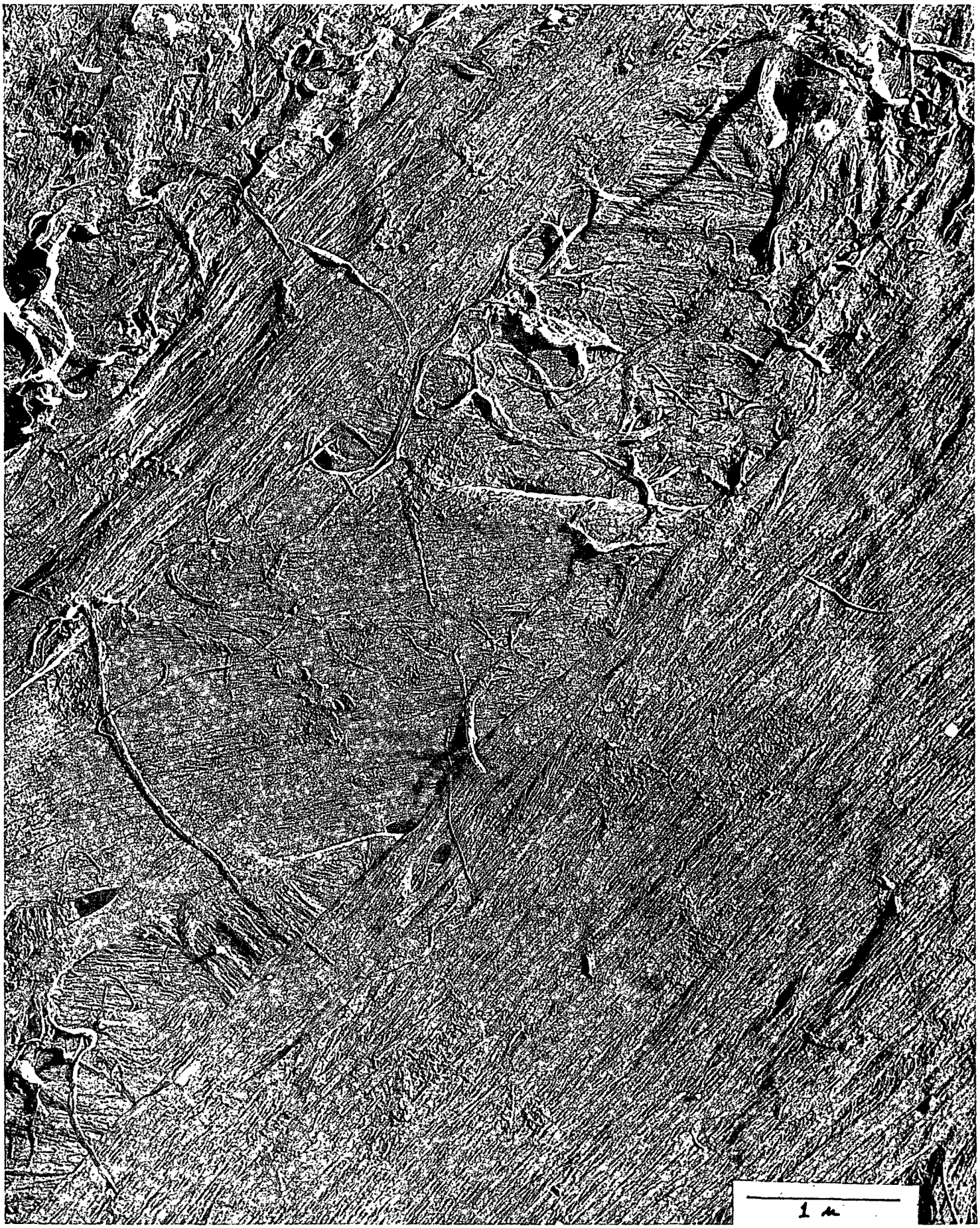

Figure 31. Electron Micrograph of Handsheet M.S. = 0.232 (30,000X).

Figure 32. Electron Micrograph of Freeze-Dried Fiber M.S. = 0.22 (30,000X)

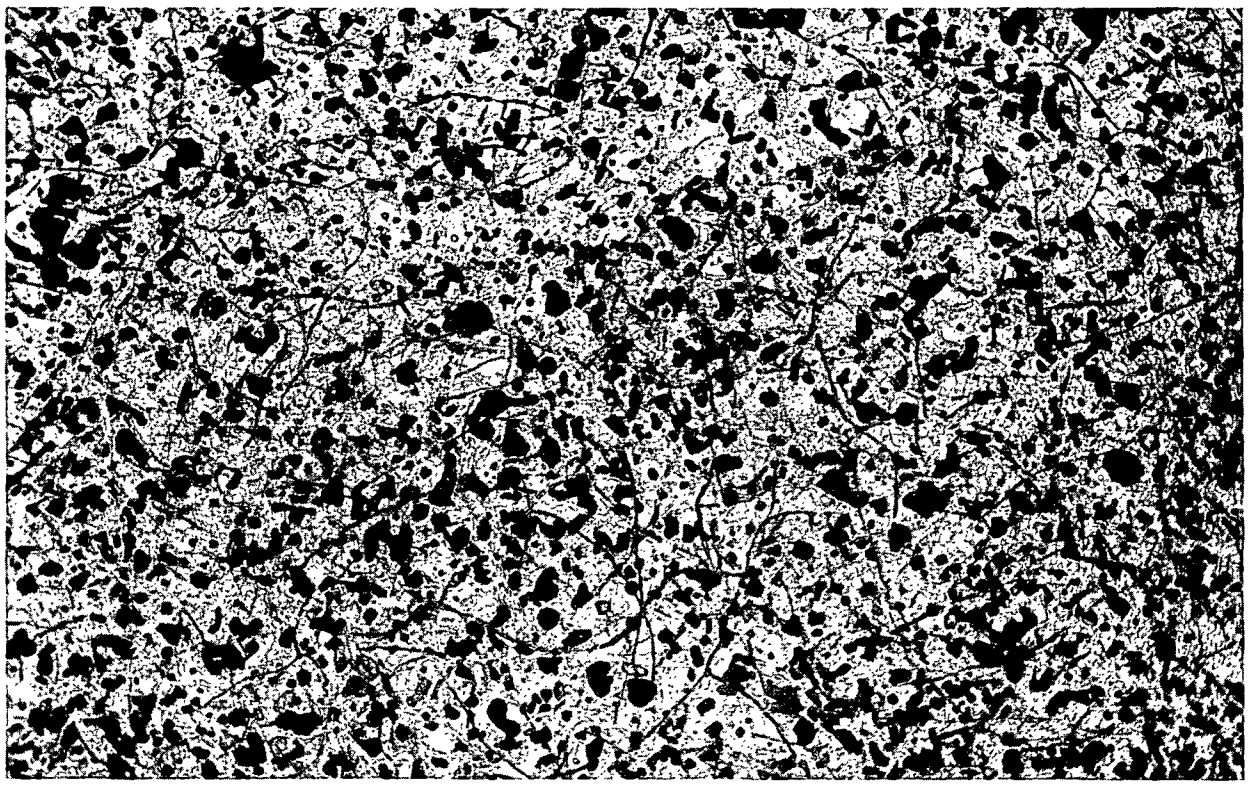

Figure 33. Mercury Intruded Sample-Untreated Control Handsheet — Mounted in Mineral Oil at 35X

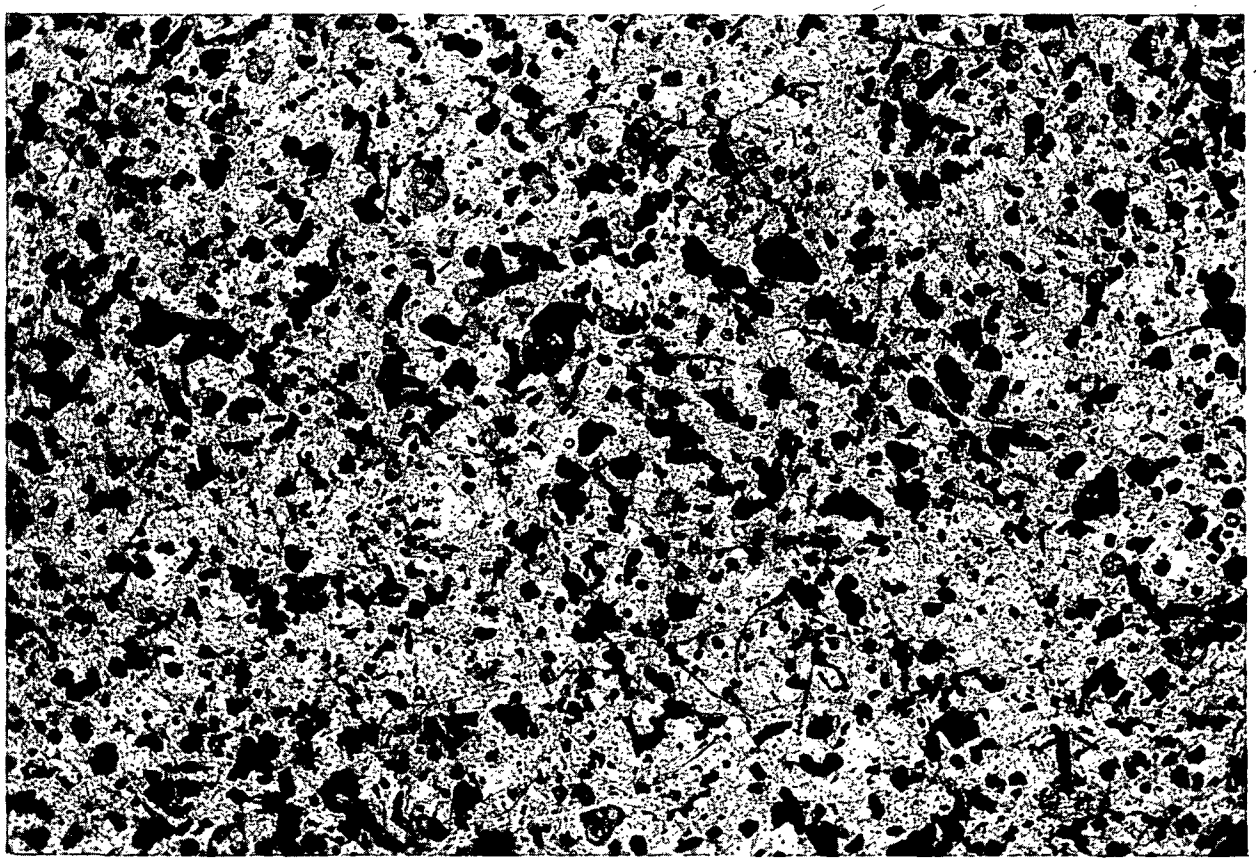

Figure 34. Mercury Intruded Sample-Handsheet with M.S. = 0.22 — Mounted in Mineral Oil at 35X

a significant increase in the sheet strength properties as well as in the IPC bonding strength and Nordman bonding strength values (Samples: M.S. = 0.220 and M.S. = 0.232). The sample with M.S. = 0.232 has about 9.0% fines which are more highly substituted (M.S. = 0.251). This sample has also a higher value of compressibility constant, M, than the one without fines. Fines in themselves are expected to be more conformable and plastic, behaving like beater additives. As such, they would provide increased molecular contact and promote the action of hydroxyethylation.

TABLE X

POROSITY DATA OF HYDROXYETHYLATED PULP HANDSHEETS

Sample, M.S.	Apparent Density, g./cc.	Bendtsen Porosity, ml./min. (air press.-150 mm. of H_2O)	Av. Pore Size Diameter, μm.
Control	0.549	1930	8.4
0.00	0.520	2530	11.1
0.22	0.589	2340	11.2

From the preceding discussions, the following major conclusions can be drawn:

1. Changes due to hydroxyethylation in fiber length distribution, formation, and fiber strength do not contribute to the observed increases in paper strength.
2. Increases in fiber-fiber bonding on hydroxyethylation are almost entirely responsible for the observed increases in paper strength. Of this, changes in the relative bonded area account for less than 10% and changes in specific bonding strength, more than 90%. This has been interpreted to mean that the major effect of hydroxyethylation of fibers is to increase the strength of the unit bonded area in paper.
3. With increased degree of hydroxyethylation, hydrodynamic properties of handsheet pulps show a continual increase in compressibility constant, M, and a

decreasing trend in specific surface area, $\underline{S}_w$. The specific volume, $\underline{V}$, decreases significantly with the first addition of ethylene oxide. The hydrodynamic properties and other evidences in the present study have been interpreted to indicate high shrinkage potential, high collapsing tendency, and increased deformability of the fibers and fibrils on hydroxyethylation. Effects of 5% alkali treatment alone were either insignificant or adverse in the present study.

4. Hydroxyethylation seems to provide a 'built-in plasticizer,' making the treated surface smoother and more conformable. This then provides extensive molecular contact and increased response to the Campbell effect during sheet-making. The more highly substituted fines appear to promote the action of hydroxyethylation.

SUGGESTIONS FOR FUTURE STUDY

1. A study of degree of collapse with extent of hydroxyethylation using Page's technique (59).
2. A study of the effects of hydroxyethylation of mercerized fibers on the bonding in paper.
3. A study of the effects of fiber species (cotton/wood) on the papermaking aspects (particularly beating) of hydroxyethylation.
4. A study of the swelling behavior of the hydroxyethylated fibers.
5. A study of the effects of clamping pressure on the zero-span tensile values of the hydroxyethylated pulp handsheets.
6. A study of the effects of beating/wet pressing on the Nordman bonding energy of hydroxyethylated pulp handsheets.
7. A study of the adsorptive potential of the hydroxyethylated fibers.
8. A study of the electrokinetic potential of the hydroxyethylated fibers.
9. A study of the papermaking properties of pulps hydroxyethylated in nonaqueous medium to the same extent as one done in aqueous medium.
10. A comparative study of the analysis of strength increase in pulp handsheets with additions of hydroxyethyl cellulose.

ACKNOWLEDGMENT

The author acknowledges with thanks the interest and assistance of the staff of The Institute of Paper Chemistry. Special credit is due to Miss O. Smith, Mrs. Margaret Malueg, Messrs. H. H. Heller, L. A. Nett, B. D. Andrews, N. L. Colson, and J. Hankey.

The author is indebted to Fox River Paper Corporation, Appleton, Wisconsin who supplied the raw combers and also provided facilities and help for the preparation of the same.

The author would also like to express his appreciation for the helpful advice and criticism of Dr. J. A. Van den Akker and of his thesis advisory committee, Dr. K. Ward, Jr., chairman, Mr. J. W. Swanson, and Dr. R. Holm.

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APPENDIX I

DEVELOPMENT OF METHOD OF PREPARATION OF UNBONDED, WATER-DRIED COMBER FIBERS ON THE IPC WEB FORMER

The classified untreated comber pulp was used for this study. The sample was first passed through a six-cut flat screen. Unbonded fibers were then prepared on the IPC Web Former. The method of formation was the same as described on page 18 except that several conditions of drying and of collecting the fibers were tried:

Identification	Nature of Drying	Method of Removal from the Drier Drum
A	Air drying[a]. Drier covered with polyethylene sheet	Brush and vacuum
B	Air drying[a]	Brush and vacuum
C	Air drying[a]	Doctor blade
D	Warm drier[b]	Doctor blade
E	Warm drier[b]	Brush and vacuum
F	Identification D fluffed in a Waring Blendor	

The above identifications along with the never-dried sample were then examined under the microscope. Photomicrographs of some of their characteristics are given in Fig. 4, 5, 34-40.

DISCUSSION OF RESULTS

Fibrillation is one of the important developments in a pulp during treatment in a beater. Examination of the photomicrographs of the never-dried pulp does reveal a large amount of fibrillation (Fig. 35). During the preparation of unbonded

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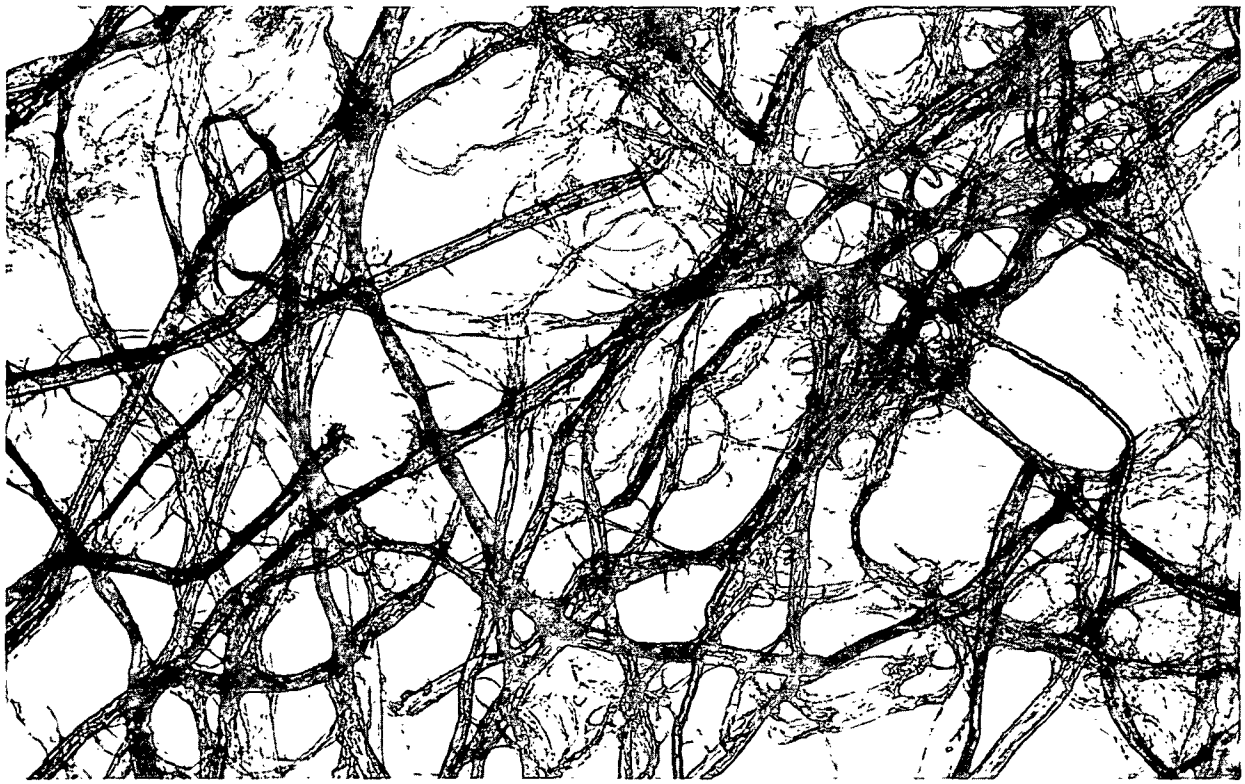
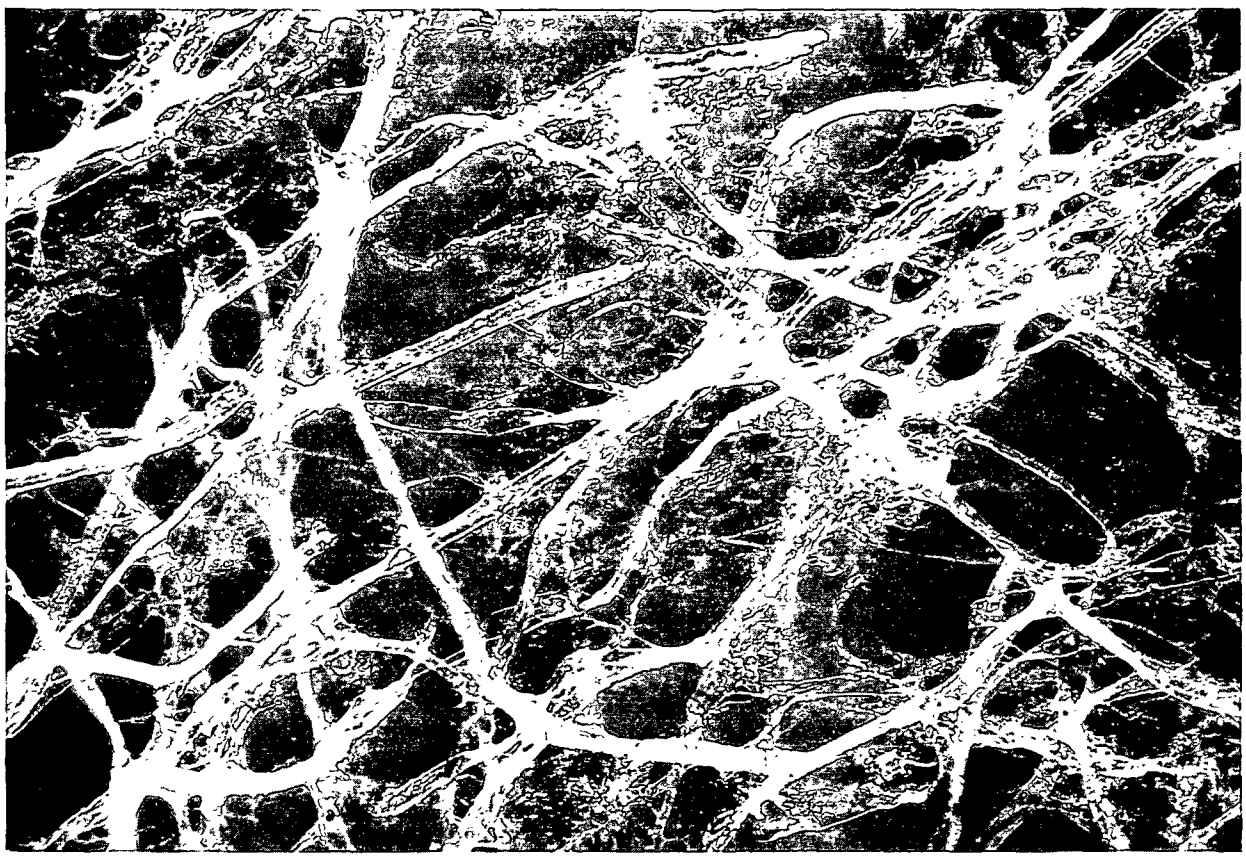
[a] The Web Former had to be run intermittently.

[b] Steam at 5 p.s.i. was opened into the drier. When warm, steam pressure reduced to less than 1 p.s.i.





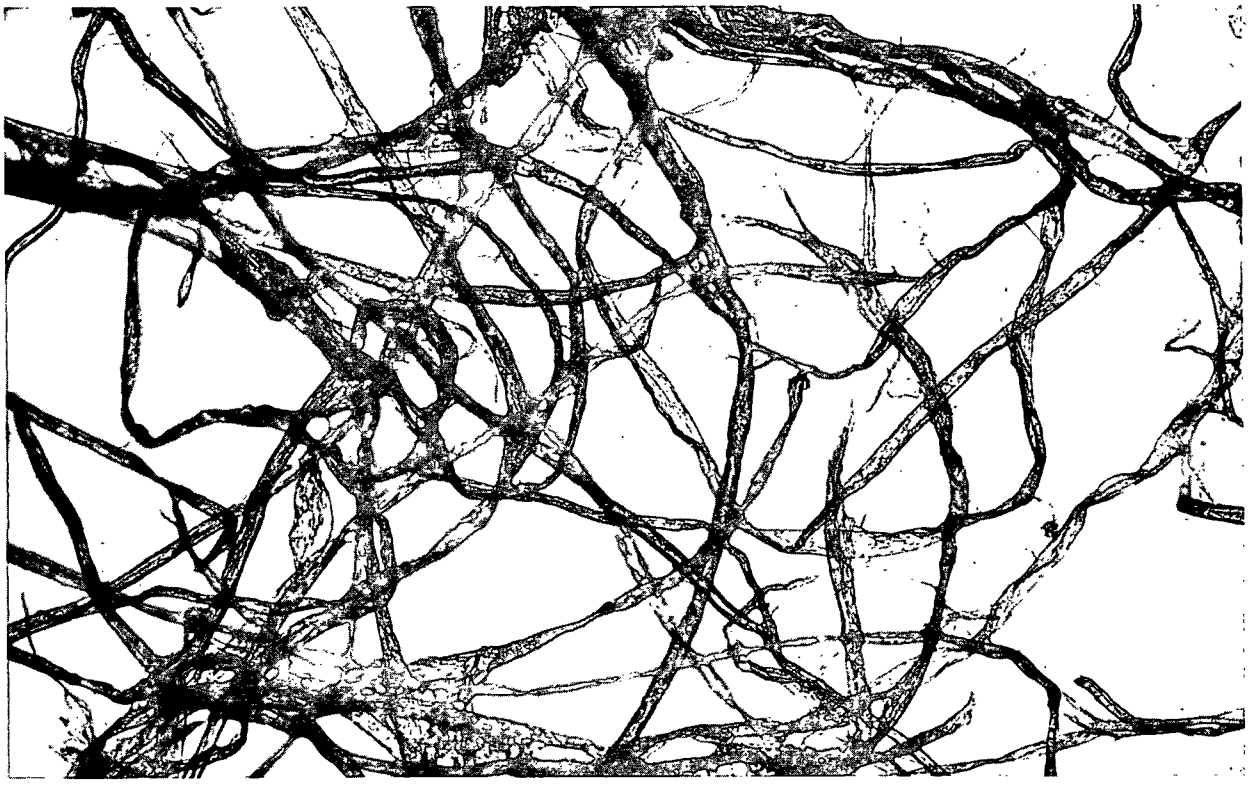


Figure 36a. Unbonded Fibers (Identification A) in Dry Mounting, Bright Field Illumination at 150X

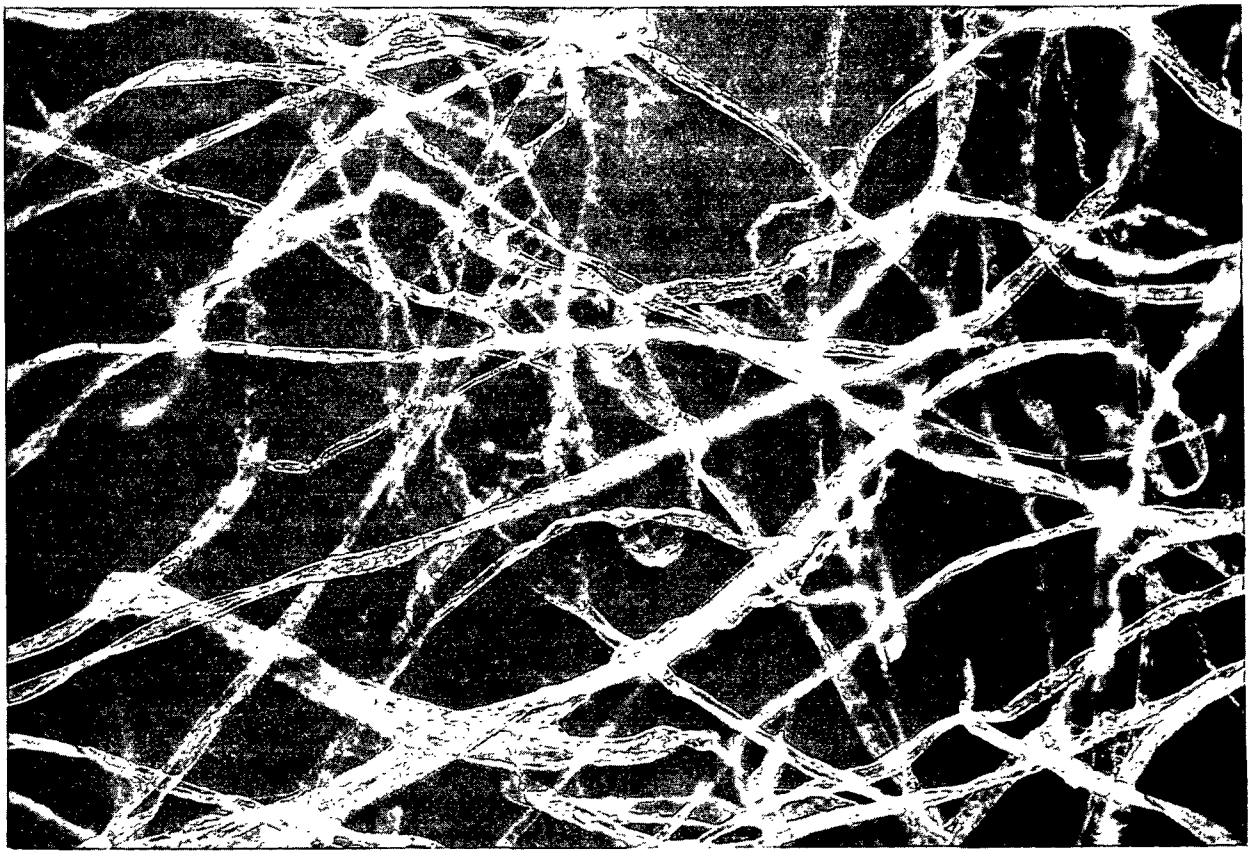


Figure 36b. Unbonded Fibers (Identification A) in Dry Mounting, Dark Field Illumination at 150X

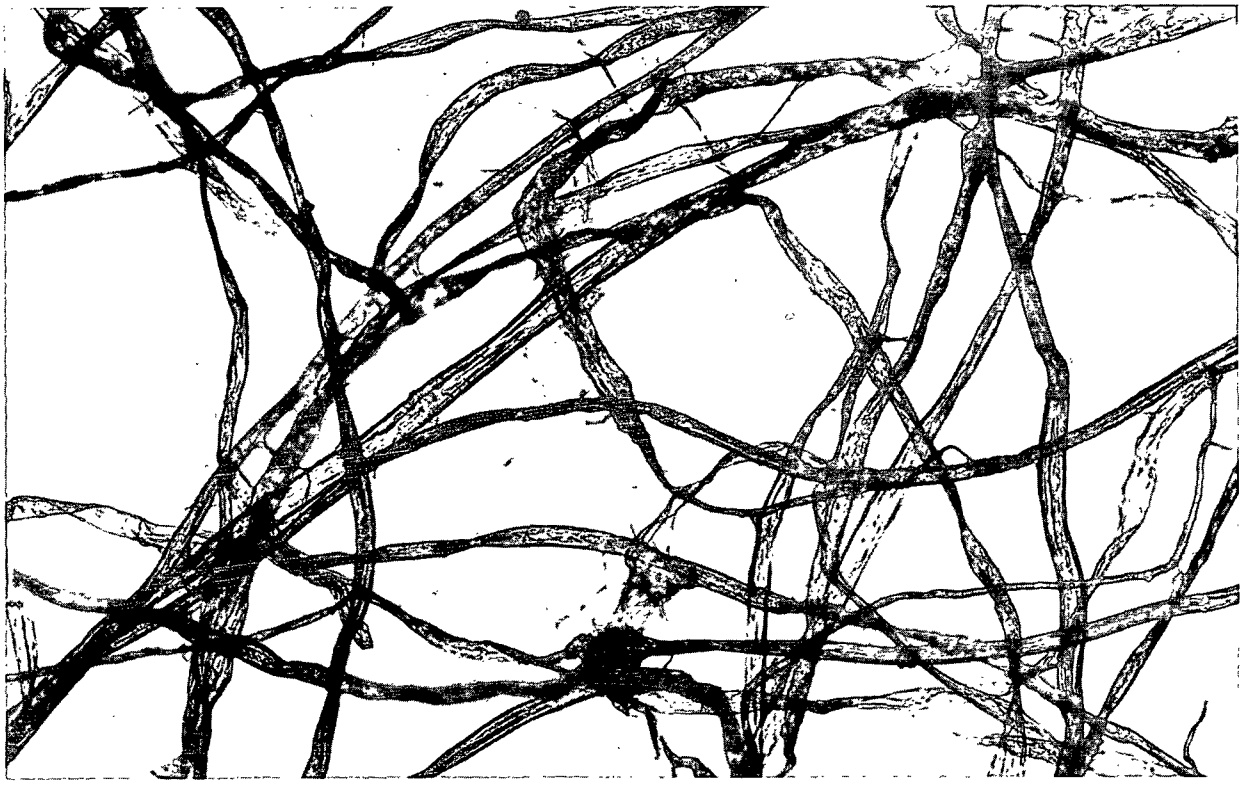


Figure 37. Unbonded Fibers (Identification B) in Dry Mounting, Bright Field Illumination at 150X

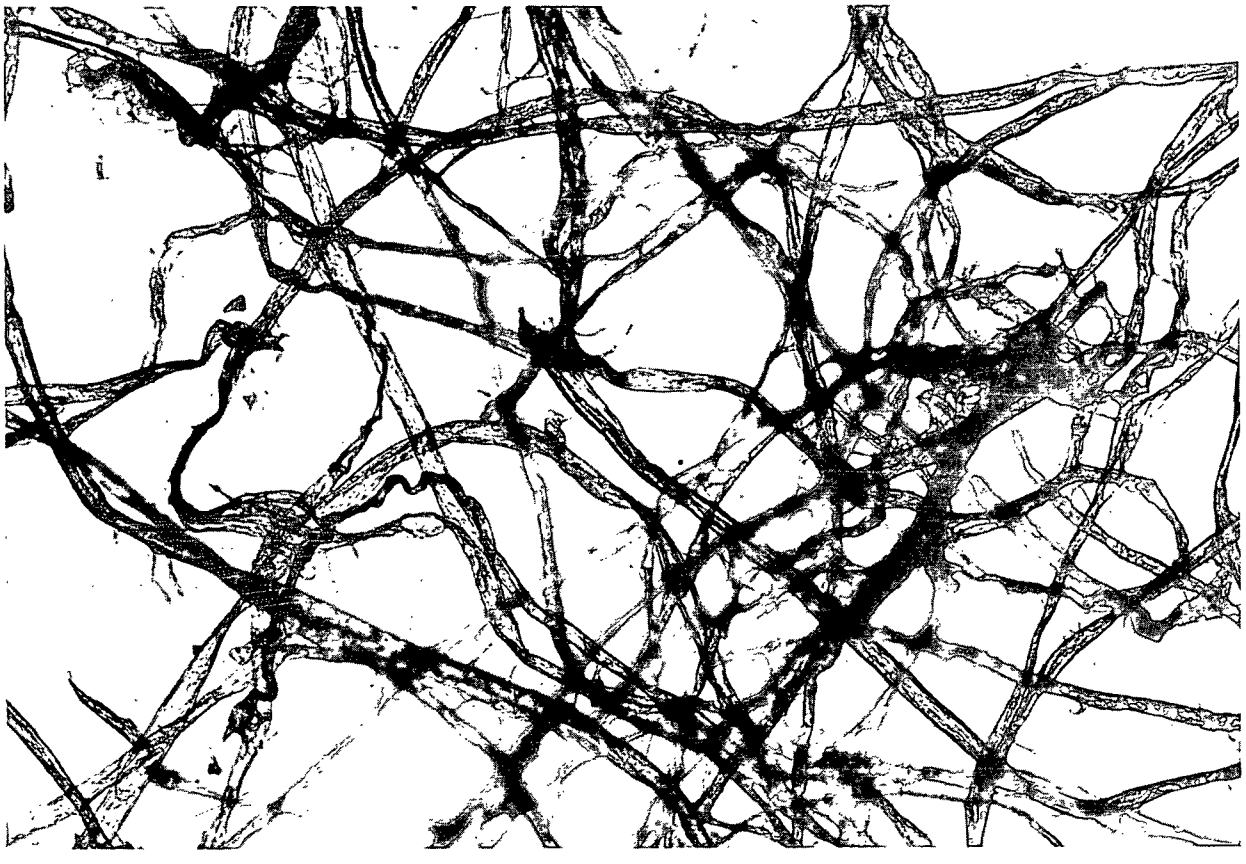


Figure 38. Unbonded Fibers (Identification D) in Dry Mounting, Bright Field Illumination at 150X

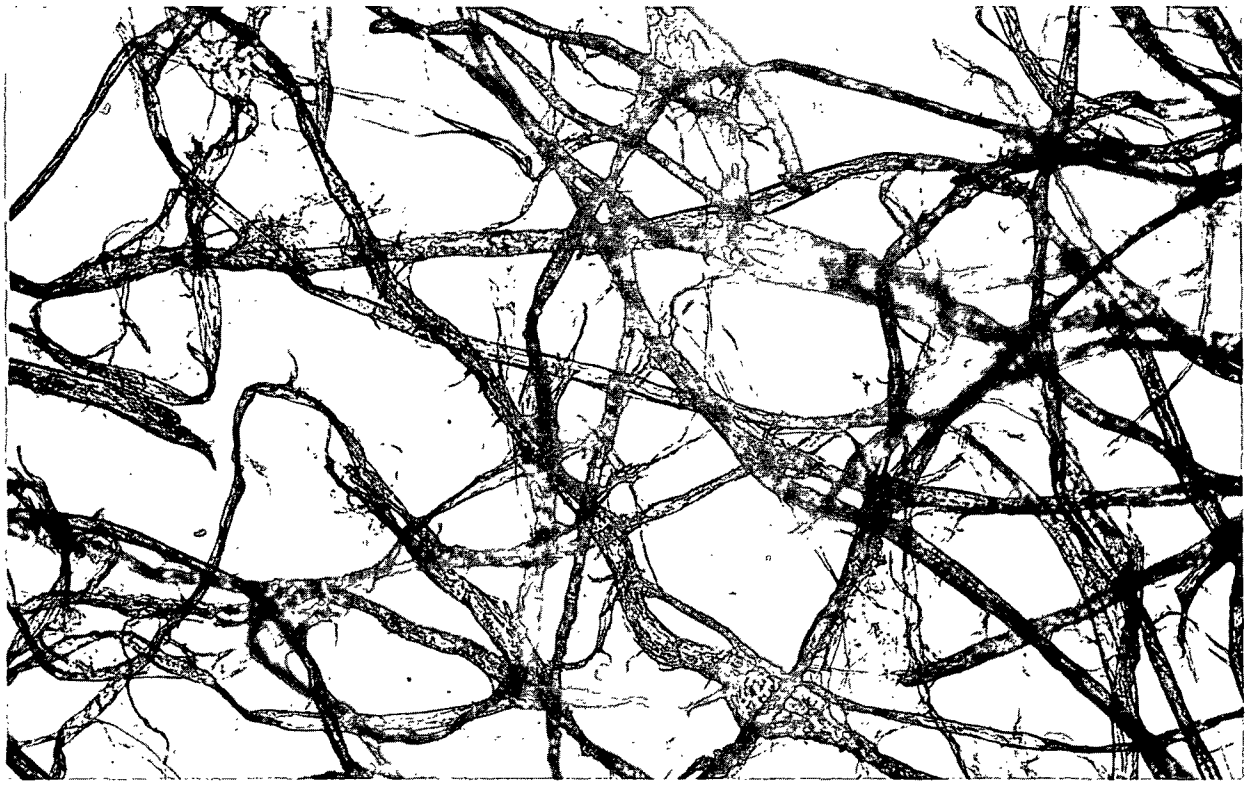


Figure 39. Unbonded Fibers (Identification E) in Dry Mounting, Bright Field Illumination at 150X

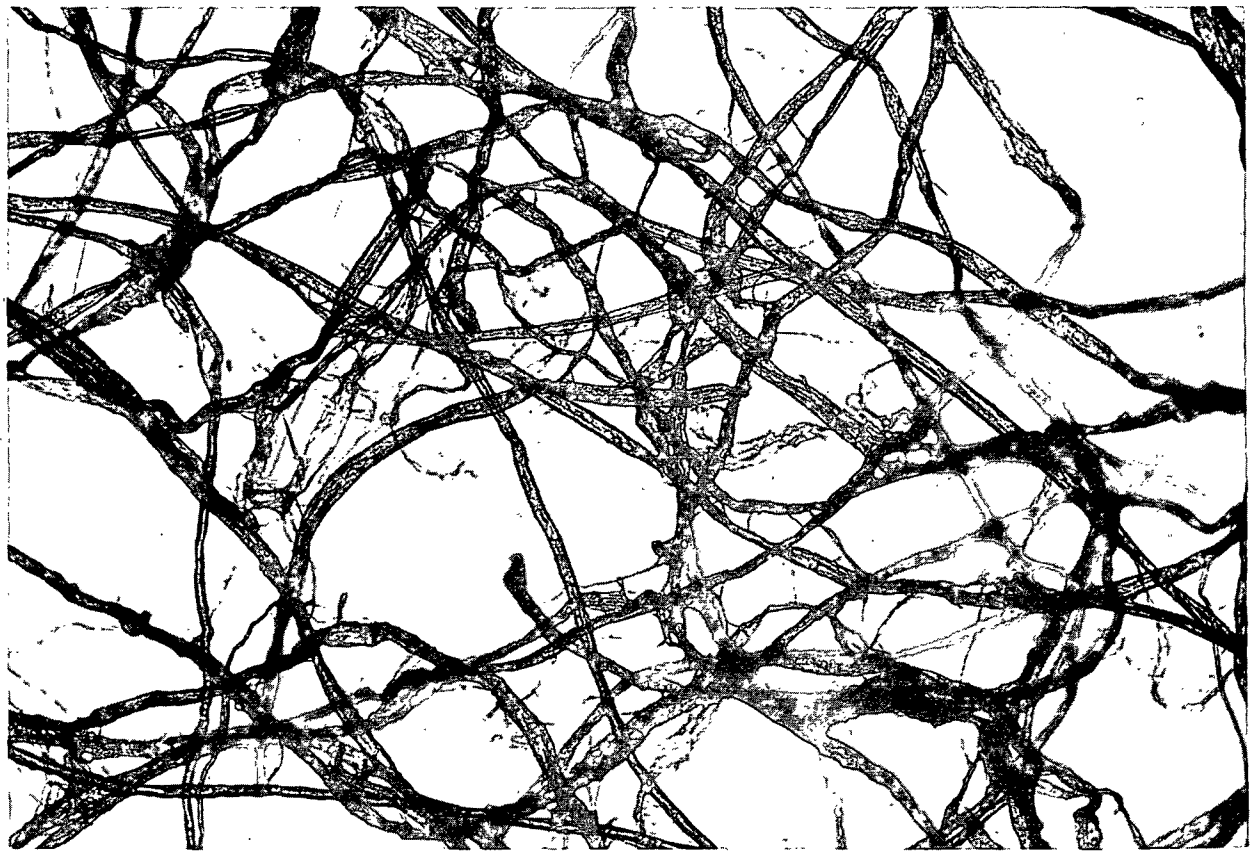


Figure 40. Unbonded Fibers (Identification F) in Dry Mounting, Bright Field Illumination at 150X

water-dried fibers, these may not completely collapse. This is particularly true for cotton and other fibers containing a very high percentage of alpha-cellulose. Here the photomicrographs of the unbonded fibers show that they had a variable amount of fibrillation depending upon the conditions used during their preparation. A cold drier drum (Identification C and D, Fig. 6a and 38) produces relatively less fibrillation, possibly because the fibrils may get disengaged or debonded from the fiber surface by adhering to the drum surface. The brush (Identification A, B, and E, Fig. 36, 37, and 39) produces a greater amount of fibrillation in the unbonded fiber samples, maybe by scratching the fiber surfaces. Moreover, the vacuum applied to collect the brushed fibers may also collect dirt from air. The use of a doctor blade seems to be better except that some fibers are creped or creased (Identification C, Fig. 6). This creping is, however, reduced to a great extent by the use of a warm drier and almost completely by fluffing the so-prepared unbonded fibers in a dry Waring Blendor (Identification F, Fig. 40).

In preliminary trials, knits or bundles of fibers (Fig. 5) were present in the unbonded fiber samples. It was thought they came from the never-dried pulp sample, so the latter was passed through a six-cut flat screen. However, the knits were still present in unbonded samples. It was found that they, to a large extent, come from the felt as a result of crushing of fibers at different stages: (1) while they are being picked up from the wire, (2) while they are being transferred to the drier. The felt must have no fibers with it when it picks up another batch from the wire.

Examination of the unbonded fibers in mineral oil or xylene showed that they are essentially unbonded.

CONCLUSIONS

From the microscopic study coupled with the operational aspect of the IPC Web Former the following can be concluded:

1. The use of a doctor blade is better than the use of a brush and vacuum for the removal and collection of unbonded fibers.
2. The drier drum should be warmed just enough to take the chill off. Apart from other advantages, this makes the process continuous and faster and avoids disturbances of conditions through interruptions. Also, creping of fibers is significantly less when a warm drier is used.
3. The unbonded fibers are essentially unbonded and clean.

APPENDIX II

PRELIMINARY STUDY OF FORMATION OF HANDSHEETS PREPARED FROM COTTON COMBER PULPS

BRITISH SHEET-FORMING APPARATUS

An attempt was made to prepare handsheets from the comber pulps on the British sheet-forming apparatus as per Institute Method 411. Instead of mechanical stirring, air agitation was done in the 'decklebox.' This was to avoid the clinging of fibers on the stirrer. Handsheets prepared this way gave formation values of not greater than 21.

EXTENDED SHEET-FORMING APPARATUS

The decklebox of the British sheet-forming apparatus was extended to a height of 214 cm. This lowered the consistency of the slurry in the decklebox during sheetmaking from 0.016 to 0.003%. Institute Method 411 was also used in this case but with the following changes: The septum was submerged slowly in water. Slurry of 0.15% consistency and containing 1.2 g. fiber (ovendry) was poured from the top. The water valve to the decklebox was opened. When the level of water was visible (at 70 cm. height) air agitation was started. When the water level reached 190 cm. height, the water valve was closed. Air agitation was continued for a total of 60 seconds. Then 15 seconds were given for air bubbles to clear away. The drain valve was then fully opened.

The sheets were taken off the septum as described in the Institute method. However, Whatman No. 1 filter paper was put in between the plate and the sheet and the sheets were wet pressed only once for 5.5 minutes (includes 1/2 minute needed to go to 50 p.s.i.). The sheets were air dried in the constant humidity room but the plate and sheet were still kept separate by the filter paper. Handsheets prepared this way gave formation values of 35-38 Thwing units.

IPC CONSTANT-RATE SHEET FORMER

The newly built IPC constant-rate sheet former (Fig. 7 and 8; p. 22 and 23) was then tried. Several preliminary trials had to be made to smooth out the operating problems:

WATER SUPPLY

In place of deionized water, softened water of 9.3 pH and 4-5°C. temperature was available. After consideration of several alternatives, it was decided to use the softened water after further conditioning it to 7-8 pH and 21-23°C. temperature.

SPECKS AND DIRT IN THE SYSTEM

This was a serious problem in the early runs. Efforts were made to clean the system; pipe lines were opened and cleaned; the water supply was filtered; the openings in the system were covered with polyethylene. All these resulted in considerable reduction of the problem. However, at the beginning of each batch, the first few sheets still showed a considerable amount of specks and dirt. The reasons were not quite clear. For some time the first few sheets were rejected.

LUMPS IN THE SLURRY

In the early trial runs, lumps in the decklebox slurry were observed. It was found that disintegration in the Williams disintegrator (36 grams o.d. fiber/6 liters of deionized water; time-10 minutes) was not good enough. The British disintegrator (method on p. 21) gave better results (Table XI). It was also seen on several occasions that the mixing of the slurry using the

recirculation pump in the pulp slurry tank created ropiness in the fibers. The use of this pump was then stopped.

TABLE XI

FORMATION VALUES:
WILLIAMS DISINTEGRATOR vs. BRITISH DISINTEGRATOR

Sheet Description	Sheet No.	Formation in Thwing Units: Williams Disintegrator	Formation in Thwing Units: British Disintegrator
Sample: untreated, unclassified, combers. Decklebox consistency – 0.004%	1	49	56
	2	50	57
	3	49	55
	4	50	56
	5	49.5	56
	Av.	49.5	56

DECKLEBOX CONSISTENCIES

In order to be able to obtain more sheets per batch, it was desirable to study whether or not a higher consistency in the decklebox could be used and still obtain the desired formation values. Handsheets were made from the untreated, unclassified comber pulp at different decklebox consistencies. Instead of the British disintegrator, the Williams disintegrator was used for slurrying the pulp. The results presented in Table XII suggest that it is better to stick to a decklebox consistency of not more than 0.004%.

TABLE XII

HANDSHEET FORMATION WITH DIFFERENT DECKLEBOX CONSISTENCIES

Decklebox Consistency, %	Formation Values in Thwing Units: Sheet No. 1	2	3	4	5	Av.
0.016	25.0	25.0	22.7	22.7	20.0	23.0
0.005	31.3	33.3	31.3	27.8	31.3	31.0
0.004	48.5	50.0	49.0	50.0	50.0	49.5

HANDSHEET MAKING PROCEDURE

The following procedure was satisfactory for making handsheets from untreated combers:

Preparation of water Preparation of slurry Handsheetmaking	As described on p. 21 and 24
Couching Pressing Drying	As per Institute Method 411. Only one pressing at 50 p.s.i. for 5 min. (plus 0.5 min. to 50 p.s.i.). The sheets dried in an atmosphere of 15±2% R.H. and 73±3°F. The sheets were pressed and dried sandwiched between blotters.

This procedure was then tried with a hydroxyethylated whole pulp sample, HE-1.5-uncl. (M.S. = 0.252). On drying, these handsheets stuck very badly to the blotters. The following series of pressing and drying conditions were then tried to overcome this problem.

Identification	Explanation	Observation
A	Blotters on both sides of the sheets. Felt side of the blotters in contact with the sheet. The directionality of the blotters in the same direction.	Sticks. Wire side of the sheet stick more.
B	Same as A but the directionality of the two blotters crosswise.	"
C	Same as A but wire side of the blotters in contact (it was difficult to say which side was felt or wire side).	"
D	Same as A but release filter paper (ink-coated) used in between the blotter and the sheet.	No sticking but ink-coated fibers transferred to the sheet.

Identification	Explanation	Observation
E	TAPPI sheets (plate in contact with the sheet during pressing and drying).	No sticking but nonuniform glaze.
F	Same as A. Blotter from the wire side of the sheet removed before drying on the rings.	Sticking on the felt side.
G	Same as A but used Whatman No. 1 filter papers in between the blotter and the sheet.	Sticking.
H	Same as A but nylon cloth put in between the blotter and the sheet.	No sticking, surface has nylon texture, also nonuniform drying.
I	Same as A but both the blotters replaced with Whatman No. 1 filter paper before drying on the rings.	No sticking.
J	Double couching with couch roll.	Sticking.
K	Double couching with plate.	Sticking.
L	Same as I but given a 2nd pressing of 2 min. after replacing one blotter with a filter paper premoistened and pressed to 50 lb. The other blotter removed before drying on rings.	No sticking.
M	The sheets were couched directly onto a millipore filter (Millipore Filter Corporation, Bedford, Massachusetts, 220 nm. pore size) backed with one thickness of a water-moistened Whatman No. 1 filter paper (moistened to minimize possible disturbance of the wet handsheet due to expansion of the filter paper). A millipore filter backed with one thickness of a water-moistened Whatman filter paper was also placed on the wire side of the handsheet. Two blotting papers were then placed on each side. The sandwiched handsheets between the plates were pressed twice at 50 p.s.i., the first pressing was for a period of 5 minutes (plus 0.5 minute to 50 p.s.i.), the second for 2 min. Between the two pressings, the blotters were changed with new ones. The handsheets were dried with the millipore filters and Whatman filter papers in contact on the drying rings.	No sticking, much smoother surface.

No sticking was observed with Identifications I, L, and M. However, Identifications I and L required considerable disturbance of the wet handsheets. Identification M was therefore chosen for handsheetmaking.

COMPARISON OF DIFFERENT HANDSHEET-FORMING APPARATUS

A classified, hydroxyethylated comber sample (M.S.-0.215) was slurried in the British disintegrator as described earlier. Then handsheets were made on the standard British sheet-forming apparatus, the extended sheet-forming apparatus and the IPC constant-rate sheet former. The couching, pressing, and (Identification I) drying method as described in the procedure on p. 25 were used and were the same for each of the handsheet-forming apparatus. Results are presented in Table XIII. They are self-explanatory.

TABLE XIII

FORMATION ON DIFFERENT SHEET MACHINES

Sheet-Forming Apparatus	Formation Values in Thwing Units					
	Sheet No.					
	1	2	3	4	5	Av.
British	20.7	21.5	20.5	21.3	21.0	21.0
Extended	34.0	31.7	32.3	33.0	34.0	33.0
IPC constant-rate	55.6	55.6	55.6	56.8	56.4	56.0

APPENDIX III

CLASSIFICATION STUDY OF SUBSTITUTION DISTRIBUTION IN AN HYDROXYETHYLATED SAMPLE

Some sort of localized difference of substitution has been observed in hydroxyethylated linters (60,61). Ward, et al. (60) has shown that an extraction with cold ethanol lowers the moles of substitution from 0.299 to 0.274, an indication that highly substituted fractions of hydroxyethyl cellulose have been removed. Gillespie, et al. (61) have obtained fractionation in hydroxyethylated samples when extracted with alkali. A sample of 0.385 M.S. on extraction with alkali of 2.75N gave two fractions, the alkali-soluble portion showing an increased M.S. of 0.404 and the insoluble fraction, a M.S. of 0.343. This study was undertaken to throw more light on the difference in substitution distribution in hydroxyethylated samples. The following were done:

1. Two methods of hydroxyethylation – in aqueous and in nonaqueous mediums – were tried.

2. (a) Samples, hydroxyethylated in aqueous medium, were fractionated and the substitution of each fraction was determined.

(b) The aqueous hydroxyethylated samples were classified and their moles of substitution were determined before and after classification.

3. One hydroxyethylated sample, from which smaller fractions were removed, was beaten in a Jokro mill for 60 minutes. The pulp was then fractionated and the substitution in each fraction was determined.

STUDY OF EXTENT OF SUBSTITUTION WITH METHODS OF HYDROXYETHYLATION

HYDROXYETHYLATION PROCEDURE

The following hydroxyethylation procedures based on the works of Gillespie, et al. (61) and Ward, et al. (60) were adopted.

Aqueous Treatment

A sample of 200 g. (o.d. comber) pulp was steeped in 3 liters of 5% NaOH (w/w) solution for 30 min. in a 7-liter stainless-steel pot. The alkali-treated cellulose was then filtered on a clean coarse-sintered glass funnel to get a press ratio of 2.6-3.0, shredded and transferred to a polyethylene bottle, which was then evacuated. Ethylene oxide equivalent to 1.5 moles/mole of anhydroglucose unit was then introduced. The bottle was then mounted on trunnions and rolled for two hours. After this the pulp was washed three times with water in the centrifuge. Then the remaining alkali was neutralized with a slight excess of approximately 5% acetic acid. The pulp was given three more washings with water in the centrifuge. The pulp was then shredded and stored in a cold room (40°F.).

Nonaqueous Treatment

Alcohol-Benzene Treatment

A sample of 200-g. ovendry standard pulp was suspended in three liters of distilled water and kept in a cold room (40°F.) for at least 18 hours. The stock was then diluted to a total of five liters and disintegrated for five minutes in Williams disintegrator. The pulp was dewatered on a Buchner funnel (without suction) and then suspended in three liters of absolute methanol. The absolute methanol was replaced with fresh methanol three times at intervals of at least 6, 6, and 12 hours. The last soaking with methanol was also for at least 12 hours. Then the methanol was replaced with benzene. Benzene was

replaced with fresh benzene three times at intervals of minimum six hours each. After the last soak with benzene (6 hours), the benzene was replaced with three liters of 2-propanol and soaked for twelve hours. At the end of twelve hours, the 2-propanol was replaced by fresh propanol and soaked for another twelve hours.

Hydroxyethylation

A 5% NaOH (w/w) solution was prepared in a solvent containing methanol and 2-propanol in a ratio of 1 to 5. The propanol-wet pulp from the previous operation was then exchanged with this alcoholic NaOH. The steeping time was thirty minutes. Then the hydroxyethylation was carried out as described under aqueous treatment. Here the press ratio was 4-4.25. The hydroxyethylated pulp was then washed three times with methanol on a Buchner funnel. The remaining alkali was then neutralized with 5% acetic acid solution. The pulp was then finally washed three times with water in the centrifuge.

RESULTS AND DISCUSSION

The results of aqueous and nonaqueous hydroxyethylation are presented in Table XIV.

TABLE XIV

AQUEOUS VERSUS NONAQUEOUS HYDROXYETHYLATION OF COMBER PULPS

	Moles of Substitution					
	Sample 1			Sample 2		
Pulp	Test 1	Test 2	Average	Test 1	Test 2	Average
Nonaqueous hydroxyethylated	0.100	0.100	0.100	0.064	0.075	0.070
Aqueous hydroxyethylated	0.220	0.217	0.218	0.262	0.276	0.269

Hydroxyethylation carried out in aqueous medium shows a considerably higher degree of substitution than the one done in nonaqueous medium. The swelling value

of cellulose in isopropanol has been found to be very low in comparison to that in water (31). In accordance with the generally accepted criteria for cellulose reaction, this low swelling of cellulose in the reaction medium should restrict the extent of etherification to the immediately accessible surface. Even keeping in mind the enhanced accessibility of the cellulose due to prior solvent exchange, it has been shown that there is almost no etherification in the absence of water (62). Reeves and Thompson (63) found the chemical accessibility for etherification with diazomethane to be 0.4% for ovendry raw cotton fibers and 0.8% for ovendry mercerized cotton fibers. When the moisture content of the fibers was raised to 6%, however, the accessibility was increased to 9.5 and 23.3%, respectively.

Quinchon (64) has shown that the dissolved ethylene oxide does not react with cellulose treated with methanolic NaOH. There are three reaction stages during hydroxyethylation: (i) the diffusion of ethylene oxide into the fibers — this depends on the nature of the solvent, (ii) the formation of the reactive intermediate ion, and (iii) the reaction of the intermediate ion with cellulose hydroxyls. According to Quinchon the presence of water is essential for the formation of the intermediate ion. Small amounts of water are undoubtedly associated with the "nonaqueous system." This could explain the extent of reaction that takes place in such a system.

FRACTIONATION STUDY OF AQUEOUS HYDROXYETHYLATED SAMPLES

Three samples hydroxyethylated in aqueous medium were fractionated on the Bauer-McNett Classifier as per Institute Method 415. A check was made on the performance characteristics of the Bauer-McNett Classifier using an hydroxyethylated pulp. The results are shown in Table XV. They indicate fair reproducibility for a particular weight of the sample used. Reported values of smaller

fractions increase when a smaller weight of sample is used. Fractions retained on 20-mesh and fractions passed through 65-mesh but retained on 150-mesh were examined for M.S. distribution. In one case, 35-mesh and 200-mesh were used instead of 20- and 150-mesh. The results are presented in Table XVI.

TABLE XV

PERFORMANCE CHARACTERISTICS OF BAUER-McNETT CLASSIFIER

	Retention, %			
Weight of Sample Used:	10 g.	10 g.	5 g.	5 g.
Retained on 20-mesh	55.81	54.90	50.98	47.06
Through 20-mesh, but retained on 35-mesh	15.40	16.95	21.16	23.44
Through 35-mesh, but retained on 65-mesh	14.20	13.82	17.12	16.42
Through 65-mesh, but retained on 150-mesh	0.42	0.42	0.40	0.39
Difference (through 150)	14.17	13.91	10.34	12.69
Total	100.00	100.00	100.00	100.00

Also, the hydroxyethylated samples prepared under the present study were tested for M.S. as such, after classification on the IPC Web Former (wire mesh – 72x56) and after handsheetmaking from the classified pulp. The results are presented in Table XVII.

The results in Table XVI show a significant heterogeneous variation of the extent of reaction. Fines are more highly substituted than the longer fiber fractions. The results in Table XVII confirm this. They indicate that classification removes certain materials high in hydroxyethyl content from the hydroxyethylated combers. Some of this loss is perhaps due to the residual glycol and other by-products, but most of it appears to arise from regions of high degree of substitution.

TABLE XVI

BAUER-McNETT CLASSIFICATION STUDY OF SUBSTITUTION DISTRIBUTION OF AQUEOUS HYDROXYETHYLATED SAMPLES

Sample Ref.	Particulars: Treatment	Cell:NaOH:Water	Overall	M.S. Retained on 20-Mesh	M.S. Through 65-Mesh and Retained on 150-Mesh
W-I[a] 27-Gv-1 5-1.5	Second cut cotton linters, 5% NaOH; 1.5 moles EnO and reaction time- 3.5 hr.	33:3:64	0.175	0.172	0.223[b]
A_3	Combers; 5% NaOH 1.5 moles EnO; reaction time- 2 hr.	30:3:57	0.218	0.211	0.235
HE-1.5	Combers; 5% NaOH 1.5 moles EnO; reaction time- 2 hr.	33:3:57	0.232	35-Mesh 0.210	200-Mesh 0.251

[a]Sample from earlier study supplied by Ward.

[b]Not enough sample for duplicate run for M.S. determination.

TABLE XVII

MOLES OF SUBSTITUTION OF UNCLASSIFIED AND CLASSIFIED HYDROXYETHYLATED SAMPLES

Sample Reference	Moles of Substitution: Before Classification	After Classification on the IPC Web Former	After Further Loss During Handsheet-making
HE-0.5	0.098	0.093	0.082
HE-1.0	0.170	0.152	0.122
HE-1.5 (unclassified)	0.252	--	0.232
HE-1.5	0.252	0.215	0.220

CLASSIFICATION STUDY OF DEGREE OF SUBSTITUTION DISTRIBUTION OF AN HYDROXYETHYLATED SAMPLE WHEN BEATEN IN A JOKRO MILL

The objective was to see if fines with different moles of substitution were produced during beating of an hydroxyethylated sample. One hydroxyethylated sample from which smaller fractions were removed was beaten in a Jokro mill for 60 minutes. The pulp was then fractionated and the substitution in each fraction was determined.

EXPERIMENTAL

Classification

An amount of 16 gram o.d. fiber sample was agitated in 2000 ml. of deionized water in the British disintegrator for 600 counts. The slurry was then divided into two batches of 1000 ml. each. One thousand ml. of deionized water was then added to each batch. Each of them was then stirred for 600 counts in the British disintegrator. The two batches were then mixed and then poured into the first tank of Bauer-McNett classifier. The wire screens of 20, 35, 65, and 200 mesh were used. The classification was carried out as per Institute Method 415. Before unscrewing the cups, another batch of 16 g.o.d. fiber sample was run the same way. After the run of two batches, the cups were unscrewed. The fractions from the wire screens of 20 and 35 mesh were mixed together and called Sample A. Sample A was not dried and was used for beating. Other fractions were dried in the oven.

A duplicate sample containing 32 g.o.d. fiber was similarly processed.

Beating in Jokro Mill

Two charges of 16 grams o.d. fiber from the above never-dried Sample A were subjected to 60 minutes beating in the Jokro mill, as per the IPC Pulping Group Procedure 58: The weighed charge was distributed uniformly in each of the

milling units (pots). Sufficient distilled water was added to each pot to bring the total weight up to 267 grams – i.e., 6% consistency. After the pots were charged, they were placed in their receptacles in the rotable disks, and their covers securely locked in place with the spanning arrangement. The milling units were spaced around the disk so that the correct balance was maintained. Then the Jokro mill was set in motion so that the milling was carried out at 150 r.p.m. The mill was run for 60 minutes and then stopped.

At the end of the beating time, the pots were removed from the mill. The milled pulp from one pot was then agitated in 2000 ml. of deionized water for 600 counts in the British disintegrator. The pulp slurry was then divided into two batches. Each batch was again stirred for 600 counts after addition of 1000 ml. deionized water. The two batches were then mixed together. This sample of 16 grams o.d. fiber was then classified in the Bauer-McNett classifier as described earlier. The second pot was also treated exactly in the same way.

RESULTS AND DISCUSSION

The results are represented in Table XVIII. They indicate that the fines are more highly substituted during hydroxyethylation but beating in a Jokro mill does not produce fines with any significantly different moles of substitution.

TABLE XVIII

BAUER-McNETT CLASSIFICATION STUDY OF DEGREE OF SUBSTITUTION OF AN HYDROXYETHYLATED SAMPLE WHEN BEATEN IN JOKRO MILL

	HE-1.5-Unclassified				Beaten Sample A			
	Retention, %				I		II	
Sample	I	II	Av.	M.S.[a]	Ret., %	M.S.[a]	Ret., %	M.S.[a]
On 35 mesh No. A	60.6	61.8	61.2	0.210	74.9	0.211	77.8	0.210
Through 35, on 65 mesh	18.1	15.3	16.7	--	12.6	--	12.1	--
Through 65, on 200 mesh	8.8	9.9	9.4	0.251	4.5	0.210	3.9	0.222

[a]Mean of two tests.

CONCLUSIONS

The present study of hydroxyethylation (with 1.5 moles of ethylene oxide per mole of anhydroglucose unit) of a 5% NaOH treated comber pulp tends to the following conclusions:

1. The extent of hydroxyethylation was considerably lower when carried out in nonaqueous medium than when done in aqueous medium.
2. The fractionation study showed that the 'fines' of the aqueous hydroxyethylated pulps were more highly substituted than the longer fiber fractions. Classification of aqueous hydroxyethylated pulps on the IPC Web Former as well as the operation of handsheetmaking removed certain material high in hydroxyethyl content.
3. Beating of a classified, hydroxyethylated sample in a Jokro mill for 60 min. did not produce fines with any significantly different moles of substitution.

APPENDIX IV

X-RAY DIFFRACTION STUDY OF HYDROXYETHYLATED PULPS

Air-dried samples were ground in a sharp, well-adjusted micro-Wiley mill to pass through a 40-mesh screen. One-inch diameter pellets were prepared from 0.50 g. of a fiber sample uniformly distributed in a piston-type mold using a total pressure of 6000 pounds (7650 p.s.i.) for fifteen seconds. These pellets (ca. 0.40-inch thick) were mounted by a press fit into a one-inch diameter hole in a 1/16-inch thick aluminum plate (1-7/16 by 2 inches) with one surface of the pellet flush with the top surface of the plate. This sample holder was inserted in the goniometer of the diffraction unit in a precise and reproducible position with relation to the x-ray beam.

A Norelco x-ray diffraction unit was used, operating with para-focusing geometry. K-alpha radiation was obtained from a copper target and a nickel filter at 32 kilovolts and 20 milliamperes. The collimated beam was defined by a divergence slit of 1/2° angular aperture at the x-ray part. The diffracted beam was defined by a 0.006-inch receiving slit and by a 1/2° angular aperture scatter slit. The signal of the diffraction beam was picked up by a proportional counter tube and traced by a Brown recorder.

The results are shown in Fig. 41. Sample: M.S. = 0.251 (Fines) was obtained from the fraction that passed through 65 mesh but was retained on 200 mesh during the Bauer-McNett classification of the hydroxyethylated whole pulp sample: M.S. = 0.232. The x-ray diffraction patterns do not show any significant difference with hydroxyethylation.

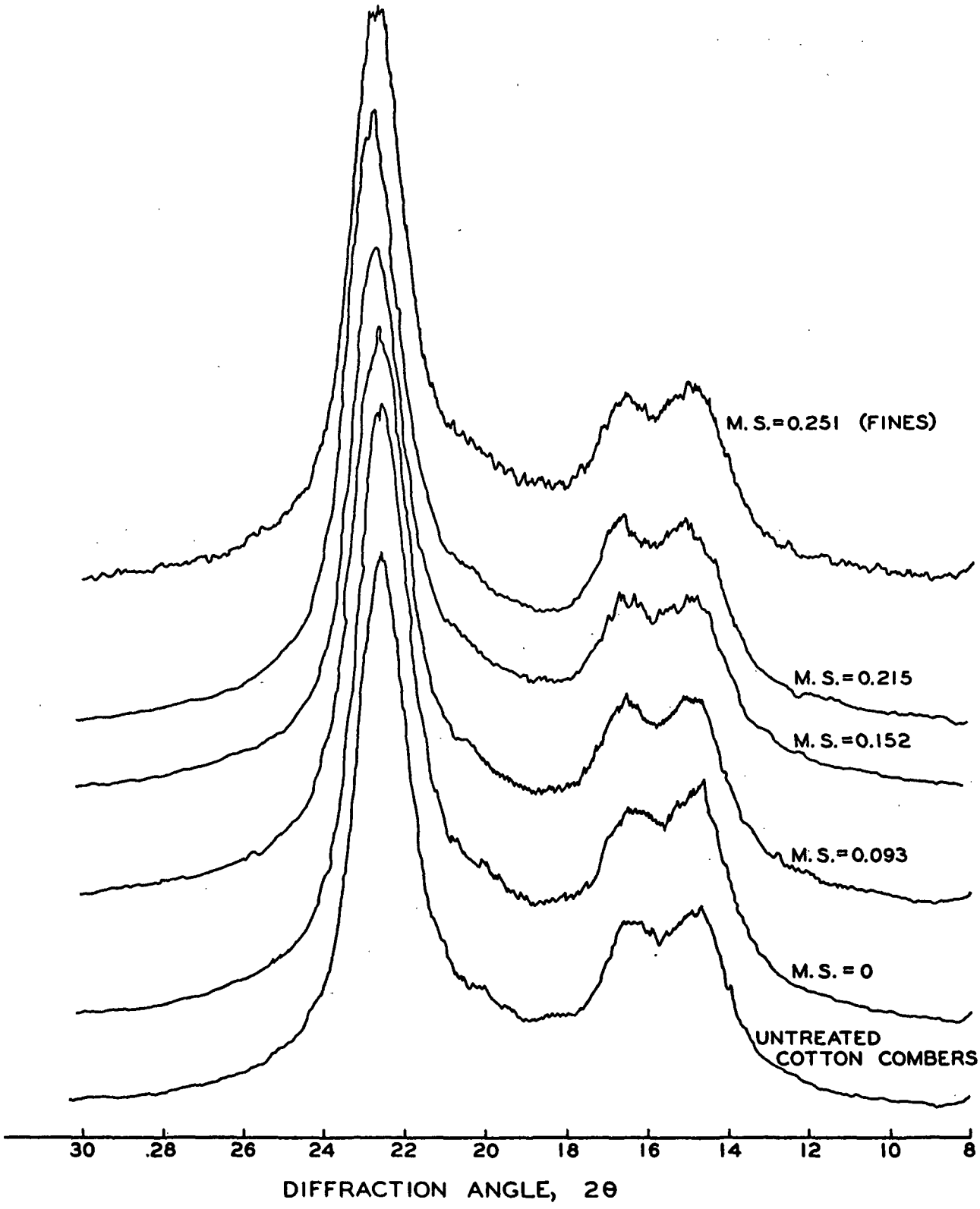


Figure 41. X-ray Patterns (Intensity Curves) for Samples of Untreated Cotton Combers and Hydroxyethylated Samples Prepared with 5% Caustic Soda

APPENDIX V

STATISTICAL CALCULATIONS

NOTATIONS

$\underline{n}$ = number of sets of observations denoted by $(\underline{x}, \underline{y})$

$\bar{\underline{x}}$ = mean value of $\underline{x}$-observations = $\Sigma\underline{x}/\underline{n}$

$\bar{\underline{y}}$ = mean value of $\underline{y}$-observations = $\Sigma\underline{y}/\underline{n}$

$\underline{c}_{\underline{xx}}$ = (original) sum of squares of $\underline{x}$-observations = $\Sigma(\underline{x} - \bar{\underline{x}})^2$

= $\Sigma\underline{x}^2 - (\Sigma\underline{x})^2/\underline{n}$

$\underline{c}_{\underline{yy}}$ = (original) sum of squares of $\underline{y}$-observations = $\Sigma(\underline{y} - \bar{\underline{y}})^2$

= $\Sigma\underline{y}^2 - (\Sigma\underline{y})^2/\underline{n}$

$\underline{c}_{\underline{xy}}$ = sum of products of deviations = $\Sigma(\underline{x} - \bar{\underline{y}})(\underline{x} - \bar{\underline{x}})$

= $\Sigma\underline{xy} - (\Sigma\underline{x})(\Sigma\underline{y})/\underline{n}$

$\underline{b}_{\underline{x}}$ = regression coefficient (slope value) of $\underline{y}$ upon $\underline{x}$ = $\underline{c}_{\underline{xy}}/\underline{c}_{\underline{xx}}$

$\underline{b}_{\underline{y}}$ = regression coefficient of $\underline{x}$ upon $\underline{y}$ = $\underline{c}_{\underline{xy}}/\underline{c}_{\underline{yy}}$

$\underline{r}$ = correlation coefficient = $\sqrt{\underline{b}_{\underline{x}}\underline{b}_{\underline{y}}}$

$\underline{s}_{\underline{o}}^2$ = variance about regression = $\dfrac{\text{sum of squares of } \underline{y} \text{ about regress.}}{\underline{n} - 2}$

= $\underline{c}_{\underline{yy}} - \underline{b}_{\underline{x}}\underline{c}_{\underline{xy}}$

$\underline{s}$ = residual standard deviation

$\underline{t}_{0.025,\varphi}$ = student t-distribution value at 95% confidence level and having φ degrees of freedom

$\underline{s}_{\underline{x}}$ = standard deviation of $\underline{x}$-observation = $\sqrt{\dfrac{\underline{c}_{\underline{xx}}}{\underline{n} - 1}}$

STANDARD ERROR

(i) for $\bar{\underline{x}}$, S.E.$(\bar{\underline{x}})$ = $\underline{s}_{\underline{x}}/\sqrt{\underline{n}}$

(ii) for a difference between two mean values $\bar{\underline{x}}_1$ and $\bar{\underline{x}}_2$, S.E.$(\bar{\underline{x}}_1 - \bar{\underline{x}}_2)$ = $\sqrt{[\text{S.E.}(\bar{\underline{x}}_1)]^2 + [\text{S.E.}(\bar{\underline{x}}_2)]^2}$

(iii) for slope value (regression coefficient) $\underline{b}_{\underline{x}}$, $S.E.(\underline{b}_{\underline{x}}) = \dfrac{\underline{s}_o}{\sqrt{\underline{c}_{\underline{xx}}}}$

(iv) for a difference between two regression coefficients $\underline{b}_{\underline{x}_1}$ and $\underline{b}_{\underline{x}_2}$:

$$S.E.(\underline{b}_{\underline{x}_1} - \underline{b}_{\underline{x}_2}) = \sqrt{[S.E.(\underline{b}_{\underline{x}_1})]^2 + [S.E.(\underline{b}_{\underline{x}_2})]^2}$$

CONFIDENCE LIMITS AT 95% LEVEL

$\pm\, \underline{t}_{0.025,\varphi}$ standard error; values of φ: (i) $\underline{n} - 1$, (ii) $\underline{n}_1 + \underline{n}_2 - 2$, (iii) $\underline{n} - 2$, (iv) $\underline{n}_1 + \underline{n}_2 - 4$.

TEST OF SIGNIFICANCE

$$\underline{T} = \frac{\bar{\underline{x}}_1 - \bar{\underline{x}}_2}{S.E.(\bar{\underline{x}}_1 - \bar{\underline{x}}_2)}$$

If $\underline{T} > \underline{t}_{0.025,\varphi}$, then $\bar{\underline{x}}_1$ and $\bar{\underline{x}}_2$ are significantly different at 95% confidence level.

NORDMAN BONDING STRENGTH

$= {}^1/_2(\underline{b}_{\underline{x}} + 1/\underline{b}_{\underline{y}})$, where the change in surface area is the independent variable ($\underline{x}$).